1. The Reactions between Ethylene and the Halogens.

2. The Absorption Spectra of Cyanogen and the Cyanogen Halides.

3. The Emission Spectrum of the Sulphur Flame.

Thesis for the Degree of

Ph.D.

by

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CONTENTS.

INTRODUCTION.

The first part of this thesis describes the reactions which take place between ethylene and the halogens, chlorine bromine and iodine. These have proved to be reactions which take place only at a surface; they do not occur in the body of the gas itself. Since the rôle played by a surface in many chemical reactions is not yet fully understood the description of the above reactions between ethylene and the halogens will be introduced by a very brief discussion of the chief features which characterise the surface reaction and distinguish it from the homogeneous or true gas reaction.

The surface reaction requires an interface between two substances in different phases whether they are in the same physical state or not. Of the different types of interfaces solid-solid, liquid-liquid, liquid-gas, etc., only the solid-gas interface will be considered here.

The reaction velocity of a surface reaction since it takes place at an interface, will depend on two factors; 1) the rate of the reaction at the interface and 2) the rate of removal of the resultants of the reaction. Both factors involve an adsorbed layer.

The speed of the reaction in the adsorbed layer depends on the concentrations of the reactants in the

layer. The 'active mass' of the reactants in a surface reaction between two gases A and B.

$$A + B \rightarrow A\,B$$

therefore, is not p_A and p_B the partial pressures of the reactants as in a homogeneous gas reaction. These quantities will be replaced by the amount of A and the amount of B adsorbed on the surface. The gas phase is not within the sphere of the reaction and therefore the pressure can only affect the rate of the reaction in so far as it alters the amount of the gases adsorbed.

In considering the various theories of adsorption one must bear in mind the following facts regarding the 'chemical' behaviour of a surface. The effect of the surface is not merely to create an increased concentration of reactants on the adsorbed layer. If this were the case all surfaces should behave equally efficiently. The action of a surface however is highly specific. For example the decomposition of alcohol on hot copper produces Acetaldehyde and hydrogen while on alumina, Ethylene and Water are produced.

Langmuir (1) has postulated that in the adsorbed layer the molecules are held by valency bonds. In this case the surface will be saturated when it is covered by a layer of molecules. A second layer might be formed in special circumstances. It has been shown

by Langmuir and others that the molecules on a monomolecular layer are all orientated. Thus in a layer of stearic acid on water, the active COOH groups are attracted towards the water while the hydrocarbon groups are orientated away from the water surface. An entirely new type of surface is therefore presented by this orientation and on this a new layer of molecules of another substance might form.

The alternative theory suggests that at the surface the gases are highly concentrated but the concentration continuously diminishes as the distance from the surface is increased, until the normal gas phase concentration is reached.

To derive an expression for the relation between the amount of gas adsorbed and the equilibrium pressure of the gas phase one of the above theories must be rejected in favour of the other . For the atmospheric theory this expression is given by the Freundlich isotherm

$$x = k\, p^{1/n}$$

where x = the amount of gas adsorbed
p = equilibrium pressure of the gas phase
k = constant
$1/n$ = fraction less than unity

k and n are functions of temperature

The reaction velocity is therefore given by an equation of the form

$$-\frac{dx}{dt} = kp^{1/n}$$

This relation is found to be true for the decomposition of formic acid on a surface of rhodium (2)

The corresponding expression for the unimolecular layer theory has been derived by Langmuir and has received the support of fact almost to the exclusion of the atmospheric adsorption theory.

If σ is the fraction of surface covered by the adsorbed gas then the amount of free surface is given by $1-\sigma$ If p is the pressure of gas in equilibrium with the adsorbed layer σ, then the rate of condensation of gas on the bare surface $1-\sigma$ is $k_1 p (1-\sigma)$ and the rate of evaporation from the covered surface σ is represented by $k_2 \sigma$. At equilibrium these rates are equal

$$k_1 p (1-\sigma) = k_2 \sigma \qquad \ldots\ldots 1)$$

$$\therefore \qquad \sigma = \frac{k_1 p}{k_2 + k_1}$$

If the adsorption is feeble then $1-\sigma \simeq 1$ and equation 1) becomes

$$k_1 p = k_2 \sigma \text{ i.e. } \qquad \sigma = \frac{k_1}{k_2} \cdot p$$

The amount of adsorption is therefore proportional to the pressure. Thus for a single gas reacting at a surface at which it is only poorly adsorbed the rate of the reaction will be proportional to the pressure i.e. the reaction follows the unimolecular law.

If the adsorption is strong $\sigma \simeq 1$ and equation 1) can be written $k_1 p (1-\sigma) = k_2$

$$\text{i.e. } 1-\sigma = \frac{k_2}{k_1} \cdot 1/p$$

In this case the amount of free space is inversely proportional to the pressure. In a reaction where a single gas is strongly adsorbed on the surface on which it is decomposed, the rate of the reaction will at first be independent of the pressure, for the surface is nearly completely covered with reactant and what is consumed by the reaction is immediately replaced by adsorption. It is only when the pressure of the gas phase becomes too small to saturate the surface that the reaction rate is proportional to the pressure. This is illustrated by the decomposition of hydrogen iodide on the surface of a heated gold wire.(3) The reaction at high pressures is of zero order but as the pressure is reduced the speed becomes proportional to the pressure of hydrogen iodide.

When two gases react at a surface the conditions at the interface are not nearly so simple. If both gases are weakly adsorbed the amount of each gas adsorbed, as in first example, is proportional to the pressure. The reaction kinetics of such a reaction will therefore be the same as if the reaction were homogeneous. The combination of ethylene and hydrogen at 250°C is an example of this type of reaction. The rate is represented by the bi-molecular formula

$$\frac{d[C_2H_6]}{dt} = k[C_2H_4]\,[H_2]$$

When one gas is more strongly adsorbed than the other the reaction kinetics are more complicated. The amount of free space, left by the strongly adsorbed gas will in this case be partly or wholly occupied by the weakly adsorbed gas. Now, it has been shown that, for a gas which is strongly adsorbed, the amount of free space is inversely proportional to the pressure, i.e. the amount of free space left for the feebly adsorbed gas is inversely proportional to the pressure. Thus if A is strongly adsorbed and B feebly adsorbed, the amount of B adsorbed is inversely proportional to the pressure of [B] and proportional to the pressure of [A]. Increase of the pressure of the strongly adsorbed gas thus causes displacement of the weakly adsorbed gas. The reaction velocity is therefore proportional to the pressure of the gas which is weakly adsorbed and within certain limits inversely proportional to the pressure of the gas which is strongly adsorbed. These limits as will be shown in an example are conditioned by temperatures and pressures at which the surface is not saturated with the strongly adsorbed gas.

Thus ethylene and hydrogen (4) combine on the surface of copper but at 20°C the reaction does not follow the bimolecular law as it does at 250°C. At 20°C the ethylene is absorbed by copper to a greater extent than hydrogen. The reaction velocity is

therefore found to be proportion to the hydrogen pressure but inversely proportional to the ethylene pressure.

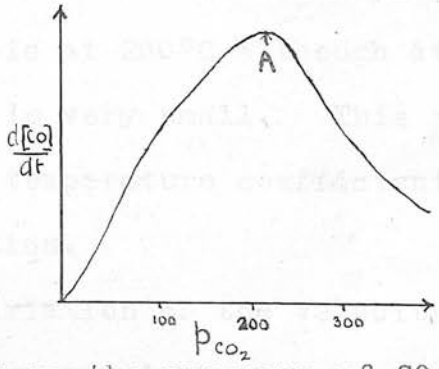
Another example of this type of reaction is that between CO_2 and H_2 on the surface of a platinum wire at 1000°C.(5)

The water formed by the reaction

$$CO_2 + H_2 \rightarrow CO + H_2O$$

was removed as soon as it was formed to reduce the back reaction to zero.

The graph shows Hinshelwood and Prichards results



This shows that as the pressure of CO_2 is increased the amount adsorbed increases and the reaction velocity is correspondingly greater. A limit A is reached, however when the surface is saturated with the mixture of the gases CO_2 and H_2 and an increased adsorption of CO_2 caused by an increased pressure, is only brought about at the expense of adsorbed hydrogen. The velocity of the reaction is thus decreased as the hydrogen is displaced from the sphere of the reaction.

Before examining the kinetics of the reactions between ethylene and bromine and ethylene and chlorine,

the heats of activation of a surface reaction will be discussed in brief.

Molecules at a surface require activation before reaction can take place in the same way as molecules in a homogeneous reaction do. Mere contact with the surface is not sufficient to start the reaction. Moreover, there is no relationship between the rate of the reaction and the amount of a gas adsorbed at the surface at different temperatures. Although ethylene is largely adsorbed on copper at 20°C, the velocity of its combination with hydrogen is not nearly so great as it is at 200°C although at this temperature the adsorption is very small. This reaction therefore has a positive temperature coefficient and therefore a heat of activation.

The variation of the velocity constant with temperature obeys the Arrhenius eqn.

$$\frac{d \log_e k}{dt} = E/RT^2$$

In the case of heterogeneous reactions E is the "apparent" heat of activation. The true heat of activation is defined as the energy which a molecule must acquire before it is in a state to undergo chemical reaction. This need not be the same as E. It is at the surface where the molecules are adsorbed that the reaction takes place but reaction velocities are calculated assuming that the whole gas phase is involved. Therefore if k is the observed velocity constant, the true velocity

constant is given by k/α, α being the proportion of gas adsorbed in the system. Now, α may vary with temperature so that $\frac{d \log k}{dt}$ will not equal $\frac{d \log k/\alpha}{dt}$ unless in the exceptional circumstance when the proportion of gas adsorbed is constant at all temperatures

Thus $$\frac{d \log_e k/\alpha}{dt} = \frac{Q}{RT^2}$$

and $$\frac{d \log_e k}{dt} = \frac{E}{RT^2}$$

Q is the true heat of activation and E the apparent heat of activation.

The relationship between Q and E can be derived for a single feebly adsorbed gas as follows :-

Using the same notation as before (eqn.I.):

$$k_1 p (1 - \sigma) = k_2 \sigma$$

Since k_2 is a rate of evaporation it may be written in the form $k_2 = C e^{- \lambda/RT}$ where λ is in this case the heat of desorption:

Substituting A for $k_1 p$ and for k_2, $C e^{- \lambda/RT}$ and since $1 - \sigma \simeq 1$, Equation 1) becomes

$$A = \sigma C e^{- \lambda/RT}$$

$$\therefore \sigma = \frac{C}{A} e^{- \lambda/RT}$$

Now $k \propto \sigma$ k/α and $k/\alpha = (e^{-Q/RT})$ const.

$$\therefore k = \frac{C}{A} e^{\lambda/RT} \text{ const. } e^{-Q/RT}$$

$$\text{i.e. } k = \text{const } e^{-(Q - \lambda)/RT}$$

$$\therefore \frac{dk}{dt} = \frac{Q - \lambda}{RT^2} \quad \text{i.e. } E = Q - \lambda$$

Thus the observed heat of activation is less than the true heat of activation by a factor which depends on the variation of adsorption with temperature.

If the reaction is retarded by adsorption of the resultants of the reaction, it can be shown in a similar way that $E = Q + \lambda_1 - \lambda$

Where λ_1 is the heat of desorption of the resultant.

The reactions between C_2H_4 and Cl_2 and C_2H_4 and Br_2 in the gas state.

Stewart & Edlund (6) studied the reaction between ethylene and bromine in order to examine the hypothesis advanced by Nef, that a compound with a double bond exists in an active and an inactive form. One of these tautomers, it is suggested, has an 'open' linkage and reaction takes place through the formation of this active molecule. These forms in the case of ethylene are represented by

$H_2C::CH_2$ $H_2\dot{C}:\dot{C}H_2$ $H_2\ddot{C}:\ddot{C}H_2$

inactive active active.

If such structures exist, it might be found that the initial velocity of the reaction between ethylene and bromine would be greater than the normal reaction velocity. This is to be expected only if the rate of the reaction between ethylene and the halogen is not greatly less than the rate at which equilibrium between the tautomeric forms is established. Stewart and

Edlund found that the initial reaction showed no abnormality which could not be explained as a wall effect. The total effect did not involve more than 1% of the ethylene present.

The rate of the reaction proved to be proportional to the concentrations of both the bromine and the ethylene. One might have expected that such a reaction as this would be homogeneous but it has been shown that there is no appreciable reaction in the gas phase even when the gases are saturated with water vapour. The addition takes place almost entirely on the walls of the reaction vessel and the rate of the reaction is proportional to the surface/volume ratio

The reaction can be explained by assuming that combination takes place in a layer of reactants adsorbed on the moist glass surface of the containing vessel. From an examination of the kinetics of the reaction :

$$\frac{-d\,[C_2H_4]}{dt} = k_1\,[C_2H_4][Br_2]$$

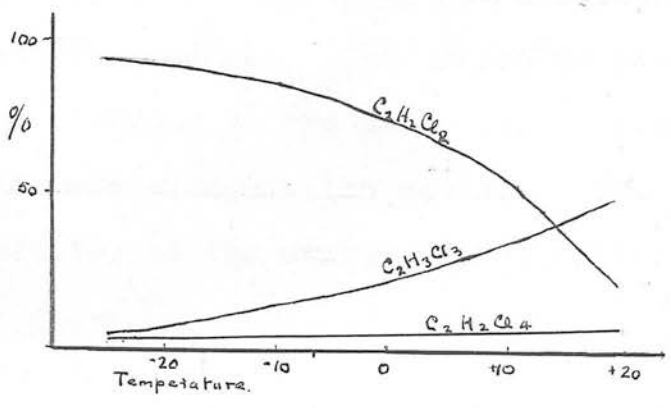
it appears that both gases are only feebly adsorbed on the surface. The effect of water is to increase the amount of gases adsorbed; this results in an increased reaction velocity. Although the catalyst for the initial reaction is a moist glass surface, the ethylene dibromide formed soon condenses out and covers the walls with a layer of liquid. The reaction is not

retarded, rather is the velocity increased. This shows that ethylene dibromide is a better catalyst than glass.

In a later paper on the combination of ethylene and chlorine, Stewart and Smith[7] show that thorough drying of the reacting gases and the reaction vessel, resulted in an induction period. Norrish[8] and Stewart and Fowler[9] have shown that this reaction also takes place on the wall surface. It is probable that the reaction starts at an active part of the surface and then is catalysed by its products or else there is a very slow reaction on a perfectly dry surface which is then accelerated by a layer of ethylene dichloride.

Stewart and Smith[10] have further shown that the ethylene chlorine reaction is not a simple addition There is also an induced substitution and there is evidence that this substitution reaction proceeds by a chain mechanism. The substitution product, $C_2H_3Cl_3$ it is postulated, is formed by the action of chlorine on an activated molecule of ethylene dichloride.

Bahr and Zieler[20] have shown how temperature influences substitution



It will be noticed that the percentage of tetrachorethane is always small, but the proportion of trichlorethane rises until at ordinary temperatures it is the principal resultant. The formation of $C_2H_3Cl_3$ is a direct substitution of chlorine into ethylene and not as might first be assumed a substitution of chlorine into $C_2H_4Cl_2$. Bahr and Zieler have shown that chlorine does not react with $C_2H_4Cl_2$ at these temperatures.

Norrish (11) has carried out experiments to find the effect of different surfaces on these reactions. He has found that the reaction velocity is dependent on the polar nature of the surface. When the walls of the reaction vessel are coated with stearic acid the reaction velocity is increased, while if paraffin covered walls are used reaction becomes inappreciable. The catalytic activity of the various surfaces for both the reactions of ethylene with chlorine and with bromine, decrease in the order wet glass, stearic acid, dry glass, cetyl alcohol, paraffin.

Norrish suggests that the molecules receive a part of their activation energy at the polar surface in the following way. The molecules constituting the polar substance create a strong but unbalanced field of force at the surface. This force in some way weakens the linkages of the molecules of adsorbed reactants and make dissociation easier. The surface thus contributes to the energy of activation in so far

as it is only these molecules which take part in the reaction. This is borne out by experiment for, although stearic acid and paraffin wax are physically similar, the reaction on the stearic acid surface is at least 1000 times more rapid than that on paraffin.

Stewart and Fowler (9) have suggested that these effects are due to the varying physical properties of the surface e.g. cetyl alcohol and paraffin wax. Moreover the paraffin may offer an unexpectedly large surface due to the lack of uniformity of the crystals and cracks etc. If a very slow reaction does exist on paraffin, the resultants would soon be present in sufficient concentration to accelerate the reaction. This would account for the induction period observed by Norrish for the ethylene bromine reaction on a paraffin surface.

In spite of this possibility it is probable that the polar nature of the surface has some of the effects suggested by Norrish although no definite mechanism for such a type of activation can be put forward until it is shown that the adsorption of the reactants on the surface is not less for paraffin than it is for the other surfaces studied.

The combination of Ethylene and Iodine is explained in detail in Part I.

As a result of the work on cyanogen and cyanogen halides, it was thought desirable to find if a

photochemical combination takes place between ethylene and these compounds. As a preliminary the absorption spectra of these substances were studied. The photochemical experiments have not yet been carried out but the photographs obtained for the absorption spectra are described in Part II.

Part III. describes a continuation of work on the spectrum of sulphur which has already been published. The paper will serve as sufficient introduction.

PART I.

E X P E R I M E N T A L.

Since the reaction

$$C_2H_4 + I_2\,(solid) \longrightarrow C_2H_4I_2\,(solid)$$

takes place with change in pressure, it can be most conveniently followed manometrically by plotting pressure decrease against time. In this case a water manometer was used for the sake of increased sensitivity. Preliminary experiments had been carried out to find if drying the reactants had any inhibiting influence on the reaction itself. Two stoppered tubes of equal size were cleaned in chromic acid, washed with distilled water and dried in an air blast. An equal weight of iodine was added to each; One of them was treated with a drop of water; the other contained a tube of fresh P_4O_{10}. They were both kept in an oven at 110°C for four days and then filled with ethylene. After 3-4 hours, it was found that combination had taken place to an almost equal extent in each tube. A third experiment employed two tubes sealed together but kept out of communication by a glass membrane which could be smashed when desired by a glass hammer contained in the apparatus. (Fig. I.)

The apparatus was thoroughly dried in an oven (110°) with P_4O_{10} in each limb. After placing 0·1 gm.

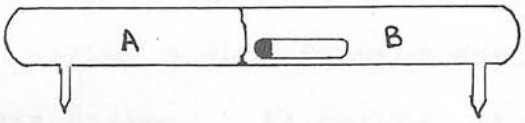


FIG. I

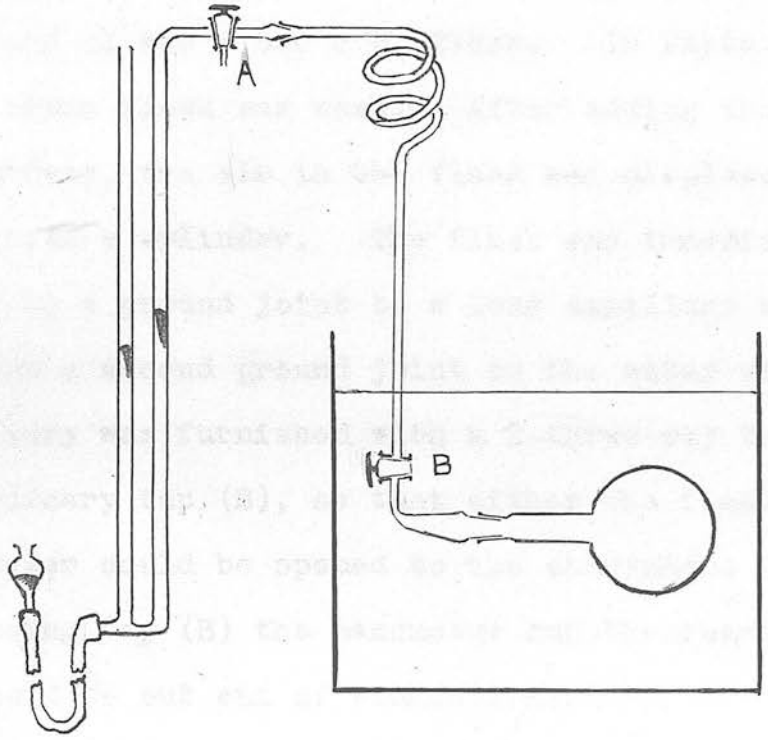


FIG. II

I_2 in A, tube A was evacuated and sealed off with a fresh portion of P_4H_{10}. B was similarly treated with fresh P_4O_{10}, evacuated and filled with ethylene to 1 atmosphere. After 3 days further drying in the oven, the membrane was broken. As before, it was found that the ethylene and iodine reacted quite readily in spite of the vigorous drying. It was therefore not thought necessary to ensure either a complete absence or a constant pressure of water vapour. A water manometer could therefore be used quite safely.

The reaction vessel in all cases except Expts. I and II was a 500 c.c. flask. In Expts. I and II a litre flask was used. After adding the iodine surface, the air in the flask was displaced by ethylene from a cylinder. The flask was immediately connected by a ground joint to a long capillary which led through a second ground joint to the water manometer. The capillary was furnished with a T three-way tap (A) and an ordinary tap (B), so that either the flask or the manometer could be opened to the atmosphere (by A), or by closing tap (B) the manometer and the reaction vessel could be put out of connection. (Fig.II)

The flask, ground joint and tap B were completely immersed in a water thermostat and kept constant at 30°C ($\pm$0·1).

The course of the reaction was followed by measuring the pressure at constant volume at regular

intervals of time. At the same time a reading of the barometric pressure was taken and any necessary corrections made.

It was found that by varying the nature of the surface quite large changes in the velocity of the reaction were obtained. Fig.III shows this clearly. The slope of curve XX gives the rate of reaction of ethylene on a glass-iodine surface of 1 gm. of moderately-sized crystals of iodine. In XVI, the same weight of iodine was used, but here the iodine surface was increased by powdering the crystals and the glass surface destroyed by coating the walls with paraffin wax. In V, the surface was formed by subliming small crystals of iodine on to the walls of the flask, while in XXIII, the whole glass surface of the flask was moistened with alcohol and drained before introducing the iodine. Tables Ia and Ib are examples of the detailed results of two experiments, while Table II gives a summary of the results obtained for a number of various surfaces.

TABLE Ia.

Expt. No. VIII.

Vol. of Ethylene = 500 c.c. at 30°C.

Wt. of Iodine = 1 gm.

Nature of surface = 1 gm. I_2 sublimed on 900 sq.cm. glass.

Time.		Pressure (cms. water)				Temperature.
Actual	Mins. from start	Right Limb	Left Limb	Barometer (m.m. Hg.)	Corrected	3·20° = 30°C
1·24		98·0	98·6	754·0	98·6	3·20
1·25	1		·9		·9	3·20
1·26	2		·9		·9	
1·27	3		·8		·8	
1·28	4		·4		·4	3·25
1·29	5		·0		·0	
1·30	6		97·6		97·6	3·30
1·35	11		94·0		94·0	
1·40	16		89·3		89·3	
1·45	21		84·2		84·2	
1·55	31		73·6		73·6	
2·1	37 A		67·2	754·0	67·2	
·7	43		62·8		62·8	3·30
·11	47		57·6		57·6	
·16½	52½		52·7		52·7	
·21½	57½		48·0		48·0	3·30
·26½	62½		44·2	754·0	44·2	
·30½	66½ B		41·0		41·0	
·37	73		36·2		36·2	
·43½	79½		32·0		32·0	
·50	86		27·8		27·8	3·30
3·00	96		23·5	754·0	23·5	
15	111		17·5		17·5	
27	123		14·5		14·5	
29	125		97·6		97·6	
31	127		97·1		97·1	
39½	135½		95·4		95·4	
50½	146½		93·1	754·0	93·1	3·30

Slope A - B = ·92 cm. H_2O/minute

TABLE Ib.

Expt. No. XXX.

Vol. of Ethylene = 500 c.c. at 21°C.

Wt. of Iodine = 1 gm.

Area of surface = 14 sq.cm. I_2 : 300 sq.cm. glass.

Time.		Pressure (cms.water)				Temperature
Actual	Time. from start	Right Limb	Left Limb	Barometer (m.m. Hg.)	Corrected	3·20° = 30°C
Friday						
2·34p.m.	-hours	90·0	90·0	741·1	90.0	21·1 A
3·37	1·05		89·7	740·4	88·8	21·1
5·03	2·5		89·3	740·0	87·8	21·1
Saturday						
11·24a.m.	20·85		78·1	737·2	72·7	21·1 B
1·29p.m.	22·9		76·6	736·5	70·3	21·1
Monday						
10·40a.m.	68·1		40·6	745·0	46·0	21·1

Slope = ·8283 cm. H_2O/hour.

Slope/Area I_2 = ·059.cm. H_2O/hour/sq.cm.

TABLE II.

Expt. No.	Iodine Surface	Other Surface	dP/dt.
			cm.H_2O min^{-1}
I	6 gm.(powdered)	450 sq.cm. glass	·42
II	5 gm.(powdered)	do.	·44
XVI	1 gm.(powdered)	300 sq.cm. paraffin	·08
XXIII	do.	300 sq.cm. paraffin + 300 sq.cm. glass	·09
XXX	do.	300 sq.cm. paraffin + 600 sq.cm. glass	·09
XX	1 gm.(crystals)	300 sq.cm. glass	·03
IV	1 gm.(sublimed)	glass 300 sq.cm.	·5
V	do.	300 sq.cm.	·5
VI	do.	600 sq.cm.	·8
VII	do.	600 sq.cm.	·75
VIII	do.	900 sq.cm.	·9
XVI	1 gm.(powdered)	paraffin 300 sq.cm.	·08
XXIV	do.	$C_2H_4I_2$ 300 sq.cm.	·14
IV	1 gm.(sublimed)	glass 300 sq.cm.	·5
V	do.	glass 300 sq.cm.	·5
XXV	do.	$C_2H_4I_2$ 300 sq.cm.	1·2
XIV	1 gm.(powdered)	Alcohol 300 sq.cm.	·80
XV	do.	do.	·6
XXIII	do.	do.	5·0

The rate of change of pressure dP/dt was obtained from the slope of the initial linear portion of the graph obtained from such tables as Ia and Ib. These graphs are fairly good straight lines for experiments with powdered iodine or large crystals, but in experiments with iodine sublimed on the walls there is a gradual falling off in speed. This is most probably

due to the gradual decrease of the iodine surface. The smallest crystals will naturally have the largest surface/mass ratio and will be used up first. The surface/mass ratio will therefore decrease as the reaction proceeds. The slowing down is not due to the back reaction ($C_2H_4I_2 \rightarrow C_2H_4 + I_2$) because the reaction was never followed very far towards equilibrium. At 30° the pressure of ethylene in equilibrium with iodine and $C_2H_4I_2$ is 18 mm. mercury. In the above experiments, the pressure of C_2H_4 was never below 700 mm. Hg. The initial curvature of the graph is most likely due to the heating of the reaction vessel and the enclosed gases. The flask was always filled with ethylene at room temperature and readings were taken immediately the flask was immersed in the thermostat. It would take several minutes for the system to get to thermal equilibrium, during which time the expansion of the gas in warming would mask the contraction due to combination. The increasing vapour pressure of ethylene diiodide as it was formed would also contribute to the curvature of the graph. At 30°C the vapour pressure of ethylene diiodide is 4 mm. H_2O, so that until this pressure had been established no contraction of the gases would take place. Since the graph was linear for periods of more than an hour, the reaction could not have slowed down to any appreciable extent during the warming up

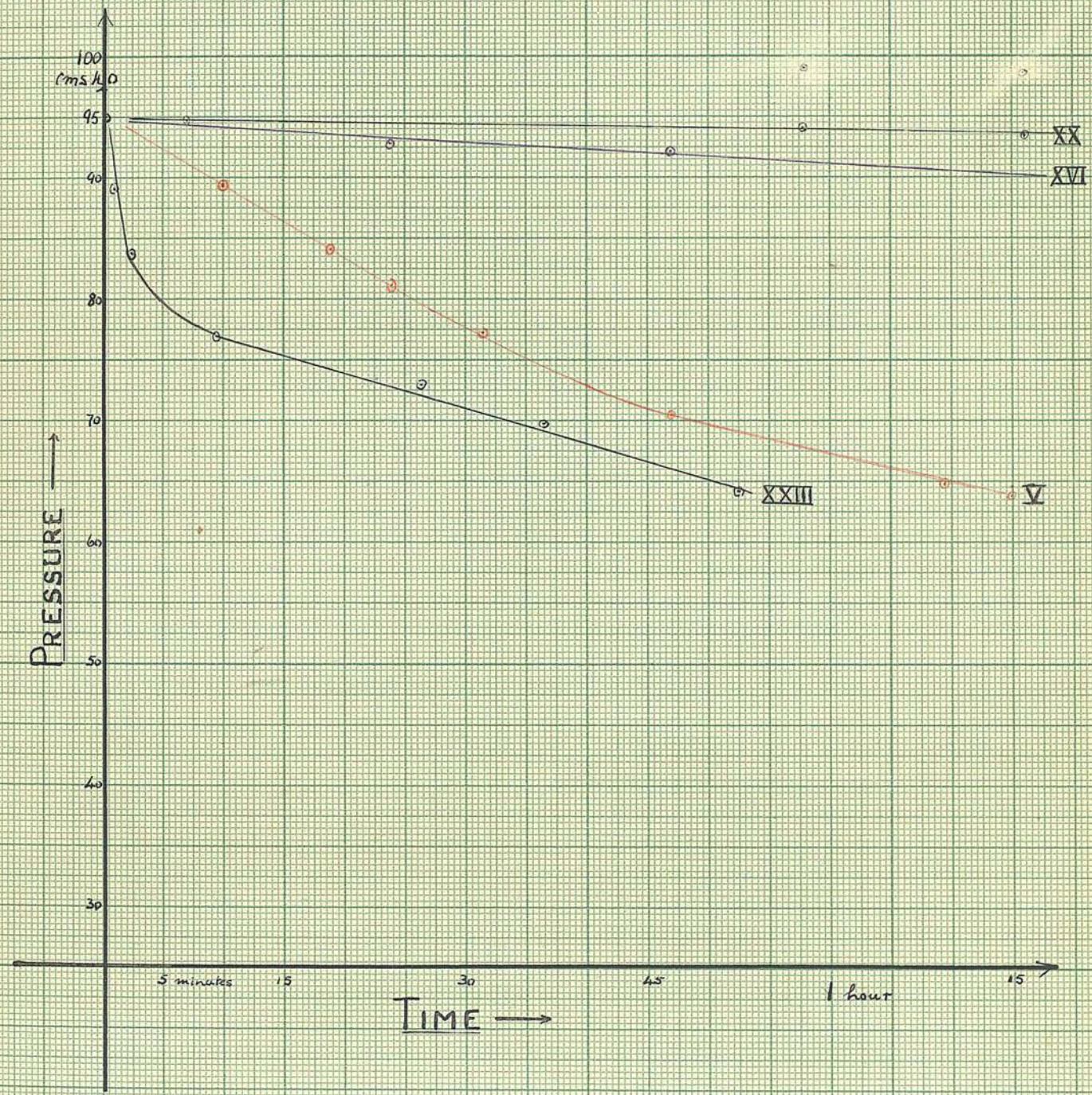
period and therefore no serious error is introduced.

Solid iodine was present in all experiments, the other surfaces studied being glass, paraffin wax, ethylene diiodide and ethyl alcohol. The glass surface was cleaned before each experiment by immersing in a chromic acid bath overnight, washing with distilled water, and drying in an air-blast. The paraffin surface was best obtained by melting about 5 grams of paraffin wax in the cleaned, dried flask and rotating in such a way that when cold the whole surface was covered with a uniform layer of the solid paraffin. Whenever an increased glass surface was required, it was obtained by adding to the flask a number of glass rods of measured surface area before filling with ethylene. In Expts. VI, VII and VIII, these rods served as the basis for the sublimed iodine crystals. To obtain a surface of ethylene diiodide, 5 gms. of the pure crystals were melted without decomposition, and the flask rotated, as in the case of paraffin, until the iodide solidified in a fairly uniform layer.

The main features of the results are noted below.

No difference is found in the behaviour of glass and paraffin surfaces. When the glass surface is introduced and increased as in Expts. XVI, XVIII and XIX, there is no corresponding increase in the velocity of the reaction. This suggests that neither

FIG. III.


100
cms H2O
95
90
80
70
60
50
40
30
PRESSURE
XX
XVI
XXIII
V
5 minutes
15
30
45
1 hour
15
TIME

glass nor paraffin surfaces can play any considerable part in the reaction.

When, however, iodine is sublimed in small crystals on to an increasingly large glass surface, which effectively increases the iodine surface, there is a corresponding increase in the speed of the reaction (Expts. IV, V, VI, VII and VIII). If powdered iodine is used (Expt. XVI) the speed is nearly ten times less than that observed when the iodine surface is increased by sublimation. The speed can be still further reduced by using large crystals instead of powdered iodine (Fig. III, Expt. XX).

It is evident that under the conditions of these experiments the reaction between ethylene and iodine must take place almost entirely at the surface of solid iodine; glass or paraffin surfaces are of secondary importance. A surface of ethylene diiodide seems to be definitely more active than either glass or paraffin, but it is very much less active than solid iodine.

The results obtained with alcohol are very irregular, due, in all probability, to the fact that the surfaces are not strictly comparable. Expts. XIV and XV contained nearly 5 c.c.'s alcohol in excess of the surface layer, while in Expt. XXIII the flask was drained and had no excess. In Expt. XXII the alcohol surface was partially dried in an air blast so that

there was probably very little alcohol present. It is obvious, however, if the above experiments are compared with Expt. XVI, that the presence of alcohol greatly accelerates the reaction. In this connection, it will be remembered that Semenow's[12] method of preparing the diiodide involves passing ethylene over iodine crystals covered with alcohol. The reaction, however, does not go to complete formation of the diiodide. All the solid iodine is used up, but equilibrium is reached before the alcohol is decolorised. The catalytic effect of alcohol is, of course, equally efficient for the decomposition of the diiodide, the crystals of which must be washed free of alcohol as completely as possible with CCl_4 or they will rapidly decompose.

Although no measurements have been made of the rate of the reaction on a glass surface alone, i.e. without the presence of a solid iodine surface, the upper limit for such a value can readily be calculated and compared with the published figures for the reactions

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

$$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$$

on wet glass surfaces.

The course of these reactions can be represented by the equation

$$\frac{-d[C_2H_4]}{dt} = k[C_2H_4][X_2] \quad \text{where } X_2 = Cl_2 \text{ or } Br_2$$

If the same mechanism is assumed for the reaction between ethylene and iodine on the glass surface, the velocity constant k can be found from the results of Expt. XX.

$\frac{-d[C_2H_4]}{dt}$ = ·022 mm. Hg/min. for the reaction on the two surfaces (1 gm. I_2 crystals and 300 sq.cm. glass) at 30°C.

(The rate of the reaction on the glass surface alone is certainly very much less than this, but this value will be taken for the upper limit.)

$[C_2H_4]$ = 761·0 mm.

$[I_2]$ = 0·5 mm. at 30°C. (Landolt Bornstein)

$\therefore k_{I_2}$ = ·022/·5 × 760 = $\underline{5{\cdot}8 \times 10^{-5}}$ at 30°C.

The velocity const. k_{Cl} for the reaction

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

was found by Norrish and Jones to be 10^{-3} at 18°C. Values for k_{Br} are given by Stewart and Edlund (10^{-2} at 0°) and by Norrish (5×10^{-2} at 0°C.).

Thus it appears that the order of the reactivity of the halogens towards ethylene on a glass surface decreases in the order $Br_2 > Cl_2 > I_2$.

In a recent paper Boer (13) has shown that iodine is adsorbed on a glass surface to a very much smaller extent than the other halogens. The adsorption is practically negligible. This would account for the

very low catalytic activity shown by glass in these experiments, and it is more than probable that the upper limit k_{I_2} calculated above is much too large.

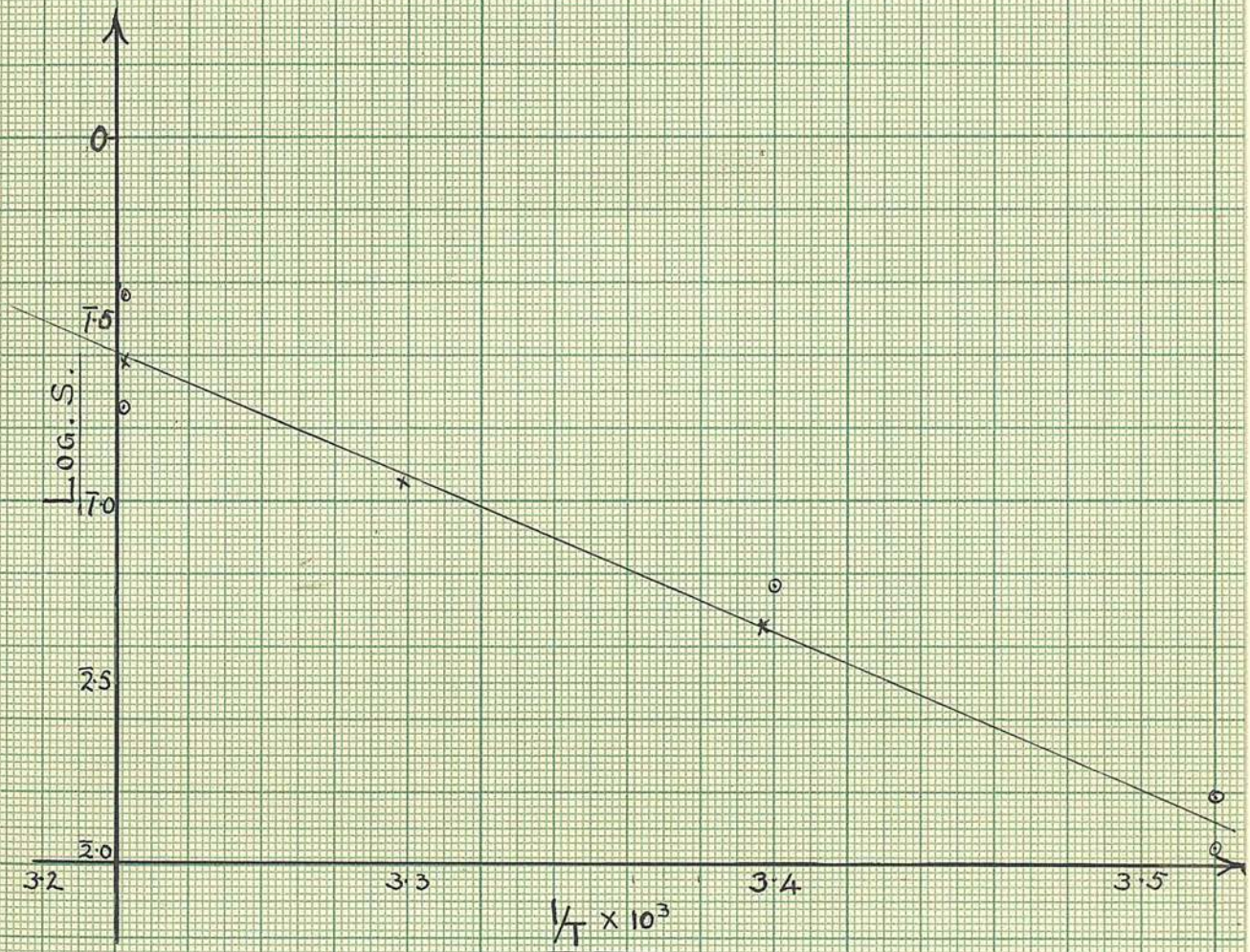
Temperature Coefficient.

The most important result of the above experiments is that the addition of iodine to ethylene takes place almost entirely on the surface of the solid iodine. To confirm this, and also to obtain a temperature coefficient of the reaction, a second series of experiments was carried out, using in this case measured iodine surfaces.

The experimental procedure was exactly the same as before except that the iodine surface was measured in the following manner. A weighed portion of iodine crystals which had been selected for their uniformity and regularity of surface were fitted as closely together as possible over a sheet of graph paper. The area covered multiplied by 2 gave a first approximation to the total iodine surface. This very approximate result would be rather lower than the actual surface area because of irregularities on the surface of the crystal, but by choosing only the most regular crystals the error was kept as low as possible and nearly equal for each individual experiment.

Values were obtained for the rate of the

FIG. V


0
$\bar{1}\cdot 5$
$\bar{1}\cdot 0$
$\bar{2}\cdot 5$
$\bar{2}\cdot 0$
log. S.
3·2
3·3
3·4
3·5
$1/T \times 10^3$

reaction per sq.cm. of iodine surface at the following temperatures, 11°C, 21°C, 30°C, 37·3°C. The results are given in Table III.

TABLE III.

Expt.No.	Temperature.	Area of I_2 surface	Rate dP/dt cm./hr.	Rate/Area cm.H_2O/hr/sq.cm.
XXVIII	11·15°C.	14 sq.cm.	·22	·015
XXIX	11·10	16	·18	·011
XXX	21·1	14	·83	·059
XXXI	21·4	16	·72	·045
XXVI	30·1	17	1·88	·11
XXXIII	37·3	17	3·1	·18
XXXIV	37·3	18	6·7	·37
XXXV	37·3	94	23·4	·25

In Fig. V. the logarithms of the rate/area is plotted against the reciprocal of the absolute temperature. The points lie on a fairly good straight line when one allows for the approximate nature of the experiment. From the slope of this curve the apparent heat of activation can be calculated.

The Arrhenius equation gives

$$\frac{d \log_e k}{dt} = \frac{E}{RT_2}$$

$$\therefore \quad \frac{d \log_e k}{d \frac{1}{T}} = \frac{E}{R}$$

$$\text{and} \quad E = 2{\cdot}3\, R \, \frac{d \log_{10} k}{d \frac{1}{T}}$$

From the graph Fig. V.

$$d \log k = 1{\cdot}30 \quad \text{and} \quad d\frac{1}{T} = 3 \times 10^{-4}$$

$$\therefore E = \frac{2{\cdot}3 \times 1{\cdot}98 \times 1{\cdot}3}{3 \times 10^{-4}}$$

$$= 19{\cdot}8 \text{ k cal.}$$

The maximum variation of E from the graph is $\pm$ 3 k cal., so that we can write

$$E = 19{\cdot}8 \pm 3 \text{ k cal.}$$

Mechanism.

There are two possible mechanisms for the reaction:

(1) The reaction takes place in the layer of ethylene adsorbed on the iodine surface.

(2) The reaction takes place between gaseous ethylene and solid iodine at the moment of impact.

If the latter is the true mechanism, the energy of activation could be calculated, assuming that all the energy of activation is supplied by the kinetic energy of the ethylene molecules, from the efficiency of the collisions of the ethylene molecule on the iodine surface.

If Z_0 molecules of ethylene collide with the iodine surface per second, the fraction of Z_0 which will have an energy greater than E is given by the expression $Z_1 = Z_0 e^{-E/RT}$.

$$\text{Hence, } \ln \frac{Z_1}{Z_0} = \frac{-E}{RT}$$

where

$$\frac{Z_1}{Z_0} = \frac{\text{no. of molecules reacting}}{\text{no. of molecules striking surface}}$$

Taking, for example, Expt. XXX, Table III,

Rate = ·83 cm./hr. Temperature = 21·1°C.

Area of I_2 surface = 14 sq. cm.

Vol. of ethylene = 500 c.c. Mean Pressure = 740 mm.

∴ No. of molecules C_2H_4 in the flask = nV_{NTP}

(where n = no. of molecules/c.c. at N TP)

$$= 2{\cdot}707 \times 10^{19} \times 500 \times \frac{273}{294} \times \frac{74}{76}$$

$$= \underline{1{\cdot}22 \times 10^{22}}$$

$$\text{and no. of molecules reacting/hour} = \frac{1{\cdot}22 \times 10^{22} \times {\cdot}83}{760 \times 13{\cdot}6}$$

$$= \underline{\underline{{\cdot}983 \times 10^{19}}}$$

The no. of collisions/hr. with the iodine surface was calculated as a 1st approximation as follows: assume a prism mounted on the iodine surface, with base equal in area to the iodine surface area and height equal to the distance travelled by an ethylene molecule per hour, i.e. equal to the velocity of C_2H_4 molecule. One-sixth of the molecules in this space will strike the iodine surface per hour.

The velocity of the ethylene molecule is calculated from the kinetic energy of the molecule

$K.E._{0°} = \frac{1}{2} mv^2 = 5{\cdot}62 \times 10^{-14}$ ergs. at 0°C,

$m = 1{\cdot}66 \times 10^{-24} \times 26$ gm. ($1{\cdot}66 \times 10^{-24}$ = mass of H_2 molecule.)

Hence $v^2_{21°} = \frac{5{\cdot}62 \times 10^{-14} \times 294 \times 2}{1{\cdot}66 \times 10^{-24} \times 26 \times 273}$

$\therefore \quad v_{21} = 52960$ cm./sec. $= 1{\cdot}91 \times 1{\cdot}0^8$ cm./hr.

$\therefore$ No. of collisions with I_2 surface =

$$= \tfrac{1}{6} \text{ no. of molecules in prism}$$

$$= \tfrac{1}{6} \frac{1{\cdot}91 \times 10^8 \times 14}{500} \times 1{\cdot}22 \times 10^{22}$$

$$= 1{\cdot}166 \times 10^{28}$$

$\therefore$ Collision efficiency $= \frac{\text{no. of mol. reacting}}{\text{no. of mol. colliding with } I_2}$

$$= \frac{9{\cdot}83 \times 10^{18}}{1{\cdot}166 \times 10^{28}} = \frac{Z_1}{Z_0}$$

$$E = -2{\cdot}3 \, RT \log \frac{Z_1}{Z_0}$$

$$= -2{\cdot}3 \times 1{\cdot}98 \times 294 \times \log\left(\frac{9{\cdot}83}{1{\cdot}166} \times 10^{-10}\right)$$

$$= \underline{12150 \text{ cal.}}$$

For Expt. XXV, which had an iodine surface 5 or 6 times greater than the others, the calculation is:-

Rate = 23·4 cm./hour. Temperature = 37°C.

Area of I_2 surface = 94 sq.cm.

Vol. of ethylene = 500 c.c. Mean Pressure = 750 mm. Hg.

No. of ethylene molecules in flask at 37° =

$$2{\cdot}707 \times 10^{19} \times 500 \times \frac{273}{310} \times \frac{75}{76} = 1{\cdot}18 \times 10^{22}$$

No. of molecules reacting per hour = $\frac{1{\cdot}18 \times 10^{22} \times 23{\cdot}4}{76 \times 13{\cdot}6}$

$$= \underline{2{\cdot}66 \times 10^{20}}$$

$v_{37°}$ (calcd. from K.E.) = $1{\cdot}96 \times 10^{8}$ cm./hr.

$\therefore$ No. of molecules striking I_2 surface = $\frac{1{\cdot}18 \times 10^{22} \times 94 \times 1{\cdot}96 \times 10^{8}}{6 \times 500}$

$$= 7{\cdot}22 \times 10^{28}$$

Hence, efficiency of collisions = $\frac{2{\cdot}66}{7{\cdot}22} \times 10^{-8}$

$\therefore$ $+E = -2{\cdot}3 \times 1{\cdot}98 \times 310 \times \log\left(\frac{2{\cdot}66}{7{\cdot}22} \times 10^{-8}\right)$

$$= \underline{11950 \text{ cal.}}$$

The mean value, 12·0 k cal., is definitely lower than the heat of activation calculated from the temperature coefficient (19·8 $\pm$ 3 k cal). The expression

$\ln \frac{Z_1}{Z_0} = \frac{-E}{RT}$ is only true if the energy E is distributed between only 2 degrees of freedom of the ethylene molecule. If it is assumed that the energy is distributed among n degrees of freedom - this, for the ethylene molecule and the iodine molecule in the crystal together - the expression becomes

$$\frac{Z_1}{Z_0} = \frac{e^{-E/RT} \cdot (E/RT)^{\frac{n}{2} - 1}}{(\frac{n}{2} - 1)\ !}$$, the

contracted form of the integral;

$$\frac{1}{\Gamma(\frac{1}{2}n) \cdot (RT)^{\frac{1}{2}n}} \int_E^{\infty} e^{-E/RT} \cdot E^{\frac{1}{2}n - 1} \cdot dE$$

which represents the chance that a molecule possesses an energy greater than E among n degrees of freedom. (See Hinshelwood).(14)

This equation was solved graphically by plotting a series of graphs for various values of n for the equation,

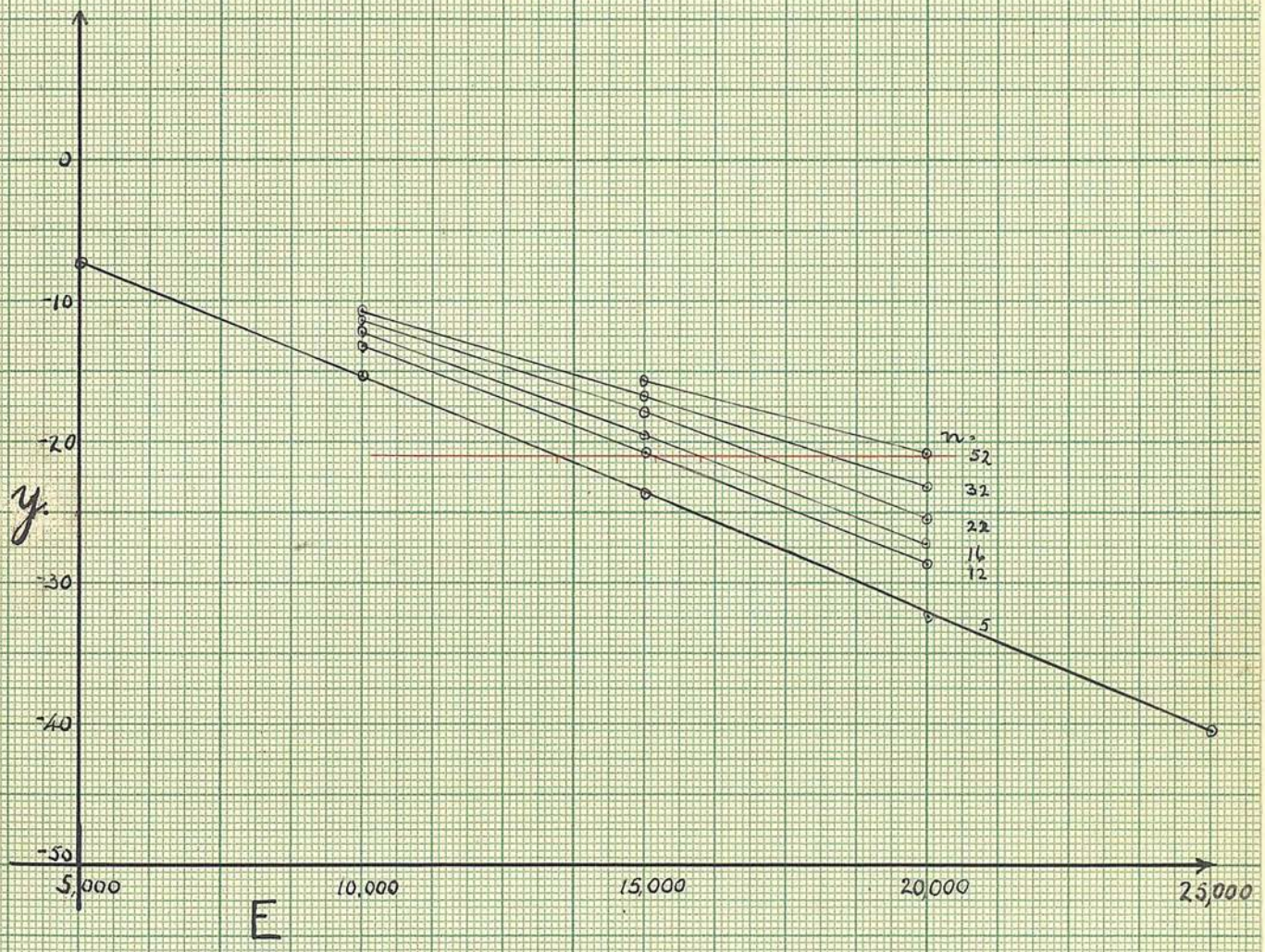
$$y = 2{\cdot}3 \left\{ -E/RT + (\frac{n}{2} - 1)\log E/RT - \log(\frac{n}{2} - 1)! \right\}$$

where E is the variable.

The graphs are shown in Fig. VI. and are plotted for n = 5, 12, 16, 22, 32, 52.

It will be seen from the graph that in order to raise the heat of activation calculated from collision efficiency to the mean value found from the temperature coefficient, it is necessary to assume 50 degrees of freedom. The molecular heat of ethylene is 11·3 k cal (15) and the atomic heat of solid iodine 6·6 k cal. This indicates 11 and 7 active degrees of freedom for ethylene and iodine respectively. The total n = 18 is hardly sufficient to raise the value of E to the

FIG. VI



neighbourhood of that calculated from the temperature coefficient. It is therefore unlikely that this is the true mechanism for the reaction. More probably the addition takes place in the layer of ethylene adsorbed on the surface of the iodine crystals. *

It is difficult to say whether the reaction on the surface is a simple addition reaction or whether it goes by means of iodine atoms, and the free radical C_2H_4I, as Schumacher (16) has shown for the homogeneous reaction in solution.

A third series of experiments was carried out to find the effect of altering the initial pressure of ethylene. The experimental procedure was, in this case, slightly modified in detail. The same reaction vessel was used and 5 gm. iodine crystals formed the iodine surface in each case. The water manometer was replaced by a mercury one. The iodine was introduced into the flask which was then connected with the manometer, immersed in the thermostat and evacuated by the three-way tap. It could then be filled with ethylene to any desired pressure. To ensure that the surfaces were comparable for each series of experiments, a low pressure of ethylene was first introduced and the slow reaction measured. After not more than two hours,

* In order to maintain the equilibrium $C_2H_4 + I_2 \rightarrow C_2H_4I_2$, the decomposition of adsorbed ethylene diiodide must also be catalysed by the iodine surface.

when the iodine surface was still free from iodide, a higher pressure of ethylene was introduced, and the rate of the reaction again measured. The rate was found to be directly proportional to the ethylene pressure, as Table IV shows.

TABLE IV.

No. of Expt.	$P_{C_2H_4}$	dP/dt. mm./hr.	dP/dt/P.
XXXVIII a	360 mm.	3·0	·012
XXXVIII b	740	10·1	·014
XXXIX a	320	5·2	·016
XXXIX b	750	10·5	·014

The kinetics of the reaction is therefore given by the equation

$$\frac{-dP_{C_2H_4}}{dt} = kP_{C_2H_4}.S_{I_2}$$ where S_{I_2} is the area of the iodine surface. This resembles the kinetics of the reaction between chlorine or bromine and ethylene on a glass surface where the rate is equal to $kP_{C_2H_4}(G.P_{Cl_2}$ – or $Br_2)$, where G is the area of the glass surface.

Ethylene and Cyanogen.

Since many of the properties of cyanogen are similar to those of the halogens, some experiments have been conducted to find if ethylene will combine with

cyanogen on a surface as it does with chlorine, bromine and iodine. As in the case of the halogens, this reaction,

$$C_2H_4 + (CN)_2 \longrightarrow C_2H_4\begin{matrix}CN\\CN\end{matrix}$$

ethylene di-cyanide (succin di-nitrile)

if it takes place, will be accompanied by a decrease in pressure and it can therefore be followed as before, by plotting graphs of pressure decrease against time.

In the first experiment, which gave entirely negative results, the reaction flask was a 500 ccs flask loosely packed with glass wool. It was connected through a ground joint to a mercury manometer and to a three-way tap. A side tube of silica containing the calculated weight of mercuric cyanide was the source of the cyanogen. After evacuating the flask through the three-way tap, half an atmosphere of cyanogen was introduced by heating the silica side tube. When the system had cooled, the total pressure was made up to 1 atmosphere by introducing ethylene through the three-way tap. The flask was kept at 15°C for six weeks but no pressure change could be observed, except a few m.m. attributed to the formation of para-cyanogen.

The glass wool which had turned slightly brown was extracted with alcohol but no trace of succin-dinitrile $\begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix}$ could be found in the extract.

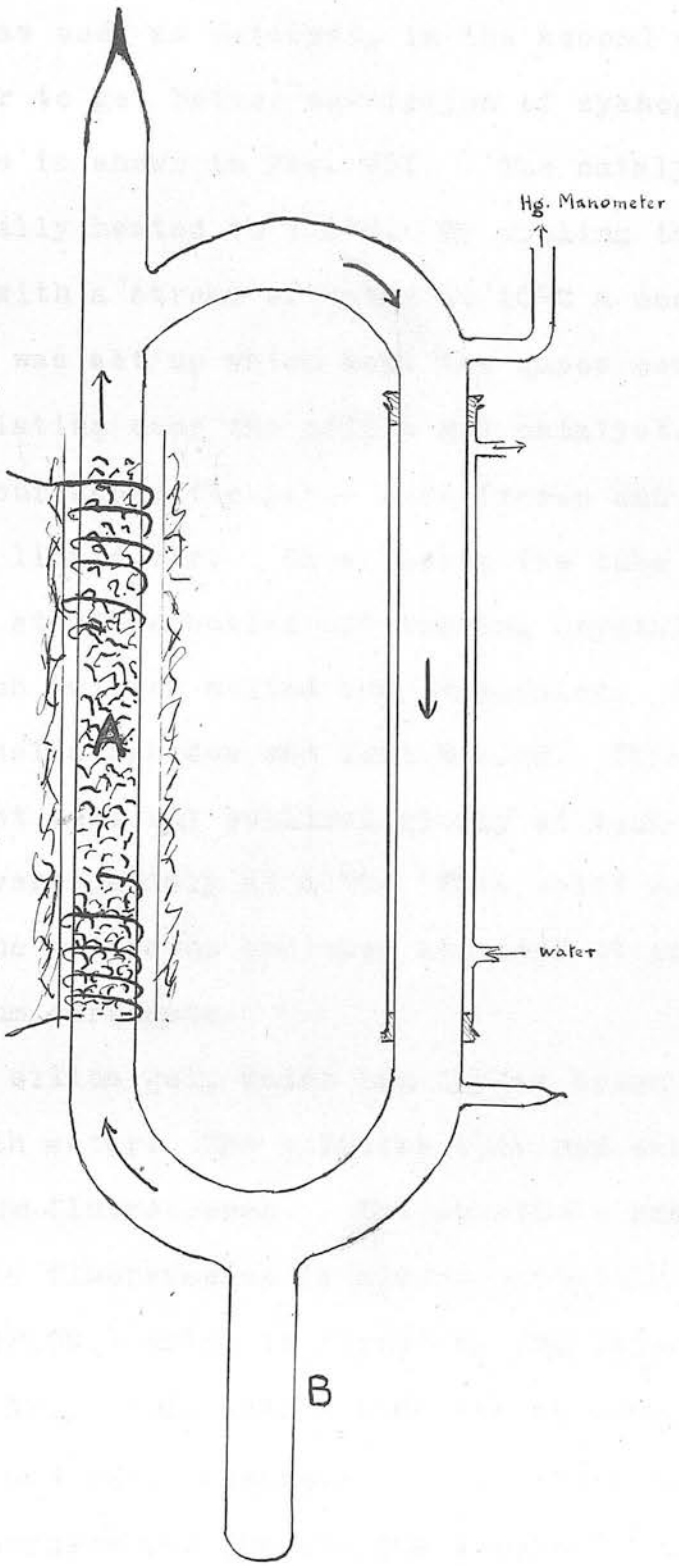


FIG. VII

This may have been due as in the case of iodine to poor adsorption of cyanogen on the glass surface. Silica gel was used as catalyst, in the second experiment in order to get better adsorption of cyanogen. The apparatus is shown in Fig. VII. The catalyst A was electrically heated to 110°C. By cooling the opposite limb with a stream of water at 10°C a convection current was set up which kept the gases continuously circulating over the silica gel catalyst. At the end of four weeks the gases were frozen out in tube B. with liquid air. On allowing the tube to warm up, the ethylene boiled off leaving crystals of cyanogen, which in turn melted and evaporated. A white crystalline solid residue was left behind. This substance did not melt but sublimed slowly at room temperature and very rapidly at 60°C. This solid was removed from the apparatus and when examined it proved to be ammonium carbamate.

The silica gel, which had turned brown was extracted with water. The solution obtained showed a brilliant blue fluorescence. The substance responsible for this fluorescence is almost certainly Azulmic acid ($C_4H_5ON_5$) which is formed by the interaction of $(CN)_2$ and NH_3. On adding NaOH the fluorescence became green and less intense. The solution was evaporated to dryness and the residue examined for succin dinitrile or its hydrolysis product ammonium

succinate by heating with zinc dust and testing for pyrrole with a shaving of red pine moistened with HCl.* A very slight reddening of the pine shaving was observed. This trace of pyrrole derivative however, is probably to be attributed to Azulmic acid rather than to a succinic acid derivative. It is clear that the reaction : -

$$C_2H_4 + (CN)_2 \longrightarrow C_2H_4 \begin{matrix} CN \\ CN \end{matrix}$$

does not take place to any appreciable extent on a glass surface at room temperature or on silica gel at 110° C.

Ethylene and the Cyanogen Halides.

A final series of experiments has been carried out to find if there is any reaction between ethylene and the halides of cyanogen. If such a reaction exists three different reaction products are possible for each halide. viz. $C_2H_4X_2$, $C_2H_4X(CN)_2$ and $C_2H_4(CN)_2$ where X is Cl, Br or I.

Preparation of Materials.

Cyanogen Chloride was prepared according to the method

---

* In order to obtain satisfactory results with the pine shaving test it was found necessary to purify the zinc dust by heating in a Rose crucible in a stream of hydrogen. If this precaution was not taken the zinc dust contained sufficient nitrogeneous and carbonaceous matter to give a positive test with the pine shaving. Using the purified Zn. dust it was possible to detect as little as .01 m.gm. of ammonium succinate. If oxalic acid is present the test is much less sensitive for the red coloration is bleached by the vapours given off the oxalic acid.

described by Held.[18] by bubbling chlorine into a solution of 26 gms KCN and 9 gm. $ZnSO_4$ in 1 litre of water kept cooled to 0^0C. After all the precipitated zinc cyanide had redissolved, just sufficient KCN solution was added to remove excess chlorine. The mixture was then warmed to room temperature and the CNCl. distilled over in a current of air, passing through a P_2O_5 tube to a receiver kept at -60^oC. The liquid was stored in sealed tubes. MP- 5^oC. B.P. 12.6^oC.

Cyanogen Bromide was prepared[19] by dropping bromine on to a saturated solution of KCN cooled in ice. The cyanogen bromide was separated into a cooled receiver by a current of warm air. The solid was kept in sealed tubes in which the crystals soon changed from white needles into transparent cubes.

Cyanogen Iodide was obtained from the laboratory stock. It was purified by recrystallisation from carbon tetrachloride and then sublimed.

Experimental. In the case of the chloride and bromide of cyanogen, a mixture of ethylene and the cyanogen halide was sealed off in a glass tube and kept in a thermostat at 37^o. The reaction between ethylene and cyanogen iodide was studied in the same apparatus as was used for the reaction between ethylene and iodine.

Results. At 37^oC no reaction was observed between ethylene and cyanogen chloride or bromide, but with

CNI a slow reaction took place, without pressure change. The products were proved to be cyanogen and ethylene di-iodide.

It is improbable that this is a direct reaction between ethylene and cyanogen iodide according to the equation

$$2CNI + C_2H_4 \rightarrow C_2H_4I_2 + (CN)_2$$

The sample of cyanogen iodide used was many years old and when the crystals were removed from the bottle they contained a large amount of iodine impurity. As they were originally pure this suggests that an equilibrium exists between $(CN)_2$ and I_2 thus

$$(CN)_2 + I_2 \rightleftharpoons 2CNI$$

The ethylene present will continuously remove the free iodine until the cyanogen iodide is completely decomposed. Such a reaction is not accompanied by any pressure change thus :

$$\underset{(1\ vol)}{(CN)_2} + \underset{(solid)}{I_2} \rightleftharpoons \underset{(solid)}{2CNI}$$

$$+$$

$$C_2H_4\ (1\ vol)$$

$$\downarrow$$

$$\underset{(solid)}{C_2H_4I_2}$$

Ethylene is replaced by an equal volume of cyanogen.

SUMMARY.

The surface reactions between ethylene and the halogens, cyanogen and cyanogen halides are described in the following summary.

1) Cyanogen iodide reacts probably indirectly with ethylene to give ethylene di-iodide and cyanogen.

2) No reaction has been observed between ethylene and cyanogen, cyanogen chloride or cyanogen bromide.

3) Ethylene reacts with iodine at the surface of the iodine crystal, to give ethylene di-iodide.

4) Ethylene reacts with bromine adsorbed on a glass surface to give ethylene dibromide.

5) The reaction between Ethylene and Chlorine is not so simple as in the case of the other halogens. With bromine and iodine only a simple addition takes place, but in the case of chlorine it has been shown that at ordinary temperatures the principal reaction with ethylene is addition and substitution together.

6) The reactions between ethylene and chlorine and bromine are irreversible reactions at ordinary temperature while the reaction with iodine reaches an equilibrium without going to complete formation of di-iodide.

The Reactions between ethylene and the halogens in carbon tetrachloride solution.

I) Ethylene and Iodine.

In contrast with the surface reaction between ethylene and iodine, in the gas state, the much slower reaction in carbon tetra-chloride solution has been found to be homogeneous at temperatures in the neighbourhood of 100°C. This reaction has been studied in detail by Mooney and Ludlam[21] and by Polissar[22] The reaction between ethylene and iodine differs from the reactions of ethylene with the other halogens in that it is a reversible reaction, equilibrium being established before complete formation of ethylene di-iodide is reached. Since ethylene diiodide is more easily purified than ethylene and also because standard solutions of ethylene di-iodide can be prepared more accurately than solutions of ethylene these investigators have found it more convenient to study the reverse reaction $C_2H_4I_2 \rightarrow C_2H_4 + I_2$ rather than the direct formation.

The method employed by Mooney and Ludlam has been to observe the rate of decomposition of a solution of ethylene di-iodide, containing varying initial concentrations of iodine, in sealed tubes at 100°C, The results they obtained are these as follows :

The reaction is autocatalytic and it was found that iodine is the catalyst.

The rate of the reaction is directly proportional to the concentration of ethylene di-iodide; it is proportional to the square root of the concentration of the iodine, or, which is equivalent, it is directly proportional to the concentration of iodine atoms thus:

$$K\,[I_2] = [I]^2$$

$$\therefore [I] = \sqrt{K}\,[I_2]^{1/2}$$

It is therefore suggested that the decomposition takes place through the agency of iodine atoms. These will therefore catalyse the forward reaction equally and the formation of $C_2H_4I_2$ will therefore be proportional to $[I_2]^{3/2}$ The kinetics of the total reaction can therefore be written

$$+\frac{d\,[C_2H_4I_2]}{dt} = k_1[C_2H_4] \times I_2^{3/2} - k_2[C_2H_4I_2] \times I_2^{\frac{1}{2}}$$

which at equilibrium is equated to zero and gives

$$K = \frac{k_2}{k_1} = \frac{[C_2H_4]\,[I_2]}{[C_2H_4I_2]}$$

Finally, Mooney and Ludlam suggest the following as two possible schemes for the reaction.

1. $C_2H_4I_2 + I \overset{a}{\rightleftharpoons} C_2H_4I_3 \overset{b}{\rightleftharpoons} C_2H_4 + I_3 \overset{c}{\rightleftharpoons} C_2H_4I_2 + I$

where either a or b is a slow reaction and the other two are instantaneous.

2. $C_2H_4I_2 + I \overset{a}{\rightleftharpoons} C_2H_4I + I_2 \overset{b}{\rightleftharpoons} C_2H_4 + I_2 + I$

where either a or b is a slow reaction.

Polissar, who also finds that the decomposition is catalysed by iodine and is proportional to the concentration of the ethylene di-iodide and the square

root of the iodine concentration, has measured the rate of the reaction at six different temperatures ranging from 40°C to 152°C. The velocity constants at the different temperatures are shown in table V.

TABLE V.

Temperature	$K_1 \times 10^4$ equiv/kg./min.
152	710
142	278
141.1	270
140.6	240
132	119
129.8	105
122	47.2
75	.28
40	.0059

When log K is plotted against 1/T the graph is a fairly good straight line; the apparent heat of activation obtained in this way is 29.0 kcal. Since the reaction goes through the agency of iodine atoms, this heat of activation (q_1) can be distributed between two components thus

$$-\frac{d\left[C_2H_4I_2\right]}{dt} = k\left[C_2H_4I_2\right]\left[I\right]$$

$$= k\left[C_2H_4I_2\right]\sqrt{K}\left[I_2\right]^{1/2}$$

$$= k_1\left[C_2H_4I_2\right]\left[I_2\right]^{1/2}$$

Hence $k_1 = k\sqrt{K}$ . . . . . (a)

k_1 is the velocity const. measured by Polissar

k is the velocity const. of the reaction $C_2H_4I_2 + I \rightarrow$

$\rightarrow C_2H_4I + I_2$

K is the equilibrium const. of the reaction $I_2 \rightleftharpoons 2I$

From (a) is obtained the equation

$$\frac{d \ln k_1}{d\, 1/T} = \frac{d \ln k}{d\, 1/T} + \frac{d \ln \sqrt{K}}{d\, 1/T}$$

$$\text{i.e.} \quad q_1 = q + \tfrac{1}{2} Q$$

The 'apparent' heat of activation is therefore made up of the true heat of activation of the reaction $C_2H_4I_2 + I \rightarrow C_2H_4I + I_2$ together with half the heat of dissociation of the iodine molecule in carbon tetrachloride solution.

Thus $q + \frac{1}{2}Q = 29,5$ kcal.

If Starck and Bodenstein's [23] value for the heat of formation of 1 gm atom of iodine in the gas phase is assumed to be nearly true for the dissociation in carbon tetrachloride solution q the true heat of activation for $C_2H_4I_2 + I \rightarrow C_2H_4 + I_2 + I$ can readily be caculated. From Starck and Bodenstein's results $Q_{132^oC} = 16.5$Kcal. q therefore is 13.0 kcal. This value agrees well with that calculated from the collision efficiency. From measurements of the variation of equilibrium with temperature Polissar found the heat of dissociation of the ethylene diiodide molecule to be 11.3 kcal.

When measuring the equilibrium constant, Polissar found that slow side reactions taking place simultaneously with the main reaction, complicate the experiment. The iodine concentration rises to a maximum and then falls slowly. The nature of these side reactions will be discussed later but the

importance of their effect on the equilibrium is at once apparent. The course of the reaction may be shown diagramatically as in Fig. IX.

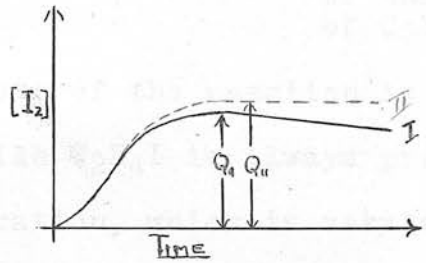


FIG. IX.

Graph I. represents the reaction actually measured while the dotted graph (II) shows the course of the simple reaction $C_2H_4I2 + I \rightarrow C_2H_4 + I_2 + I$ without the complication of any side reaction. This side reaction is taking place during the whole course of the experiment and its relative value will rise with temperature. The actual maximum yield of iodine Q_1 will therefore be less than the theoretical Q_{11} by an amount which depends on the relative importance of the side reaction and therefore, on the temperature. This introduces a double error. The actual value of Q_1 is probably too small and therefore K the equilibrium constant is too small. $\frac{dK}{dt}$ (t= temperature) will also be too small because the side reaction is becoming more important at higher temperatures.

Since Polissar's equilibrium measurements were all made at the higher temperatures 122°-152°C they are most likely too low, as also are the heat of dissociation and the heat of activation.

In a discussion of Polissar's paper Schumacher (16) prefers the scheme :-

(1) $C_2H_4I_2 + I \rightarrow C_2H_4I + I_2$

(2) $C_2H_4I \rightarrow C_2H_4 + I$ (Reactions 2 & 3 being fast reactions leading

(3) $C_2H_4 + I \rightarrow C_2H_4I$ to a rapid attainment of the equilibrium conc of C_2H_4I.

The rate of the reaction is determined by reaction (1), while C_2H_4I is always present in its equilibrium concentration, which is very small. The heat of activation of reaction (1) calculated from Polissar's results averages 11.5 Kcal ($\pm$ 2) In this case the heat of activation can be equated to the heat of the reaction (since the heat of activation of the reverse reaction is very nearly zero) we can therefore write -

$$C_2H_4I + I_2 \rightarrow C_2H_4I_2 + I + 11.5 \text{ kcal.}$$

The heat of total reaction is 11.3 kcal. which means that $Q_{C_2H_4I}$ the heat of reaction of the reaction $C_2H_4 + I \rightarrow C_2H_4I$ is very small i.e. that the C — I link in C_2H_4I is very weak.

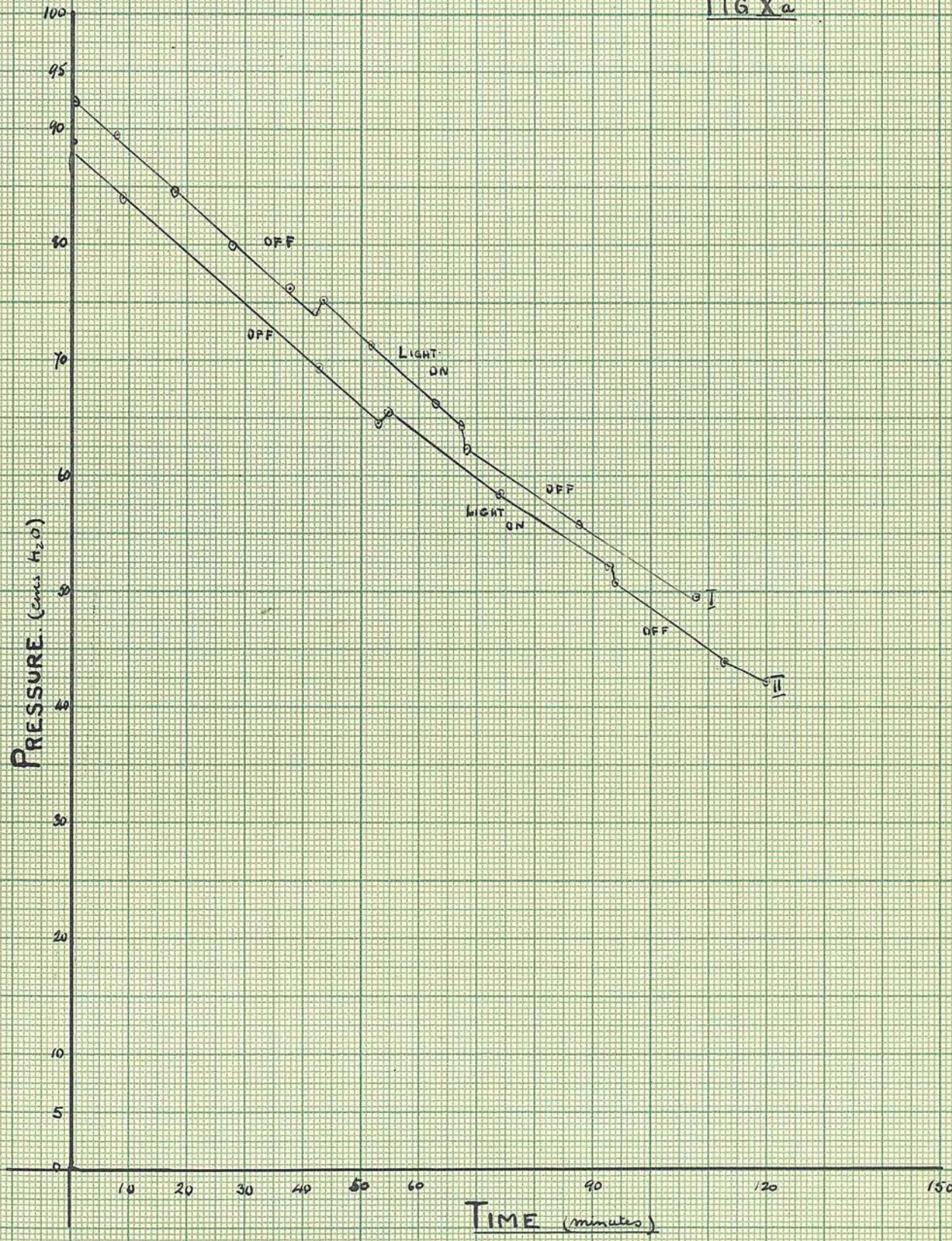
These results have been confirmed by Schumacher and Wiig [24] who studied the photochemical reaction at 100°C. The heat of activation of the total reaction was found to be 11.8kcal. Now since C_2H_4I is always present in its equilibrium concentration this activation energy applies only to the following two links in the chain :-

(a) $C_2H_4I_2 + I \rightarrow C_2H_4I + I_2$

(b) $I + I \rightarrow I_2$

(b) requires no activation energy: it is a reaction which goes through the agency of triple collisions and

FIG Xa


100
95
90
80
70
60
50
40
30
20
10
5
0
PRESSURE. (cms H_2O)
OFF
OFF
LIGHT ON
OFF
LIGHT ON
OFF
I
II
10
20
30
40
50
60
90
120
150
TIME (minutes)

in solution these are frequent. Reaction (a) therefore has an activation energy of 11.8 kcal. which is in good agreement with the thermal value.

It may be mentioned at this point that Schumacher and Wiig found that at room temperature there was no appreciable photochemical reaction, due to the energy of activation required for the reaction

$$C_2H_4I_2 + I \rightarrow C_2H_4I + I_2$$

This was also found to be true for the gas reaction. In experiments I. and II. of the previous section (Page 25), the effect of light on the rate of the reaction was studied. The reaction flask had been totally silvered on the outside, except for a small window, which was illuminated through a window in the thermostat by a water cooled mercury arc lamp. The reaction in the light was no faster than the dark reaction as the graphs (Fig. X a) show. These graphs represent the early course of the reaction but this is equally true for the reaction near equilibrium. A glass bulb containing 1gm $C_2H_4I_2$ (impure) crystals was sealed to a glass spring gauge and evacuated (Fig. X)

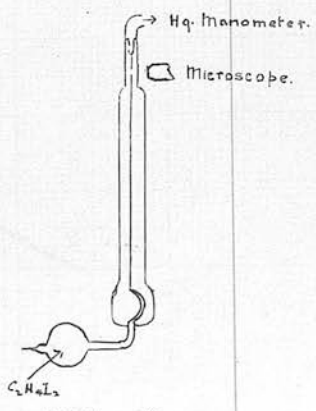
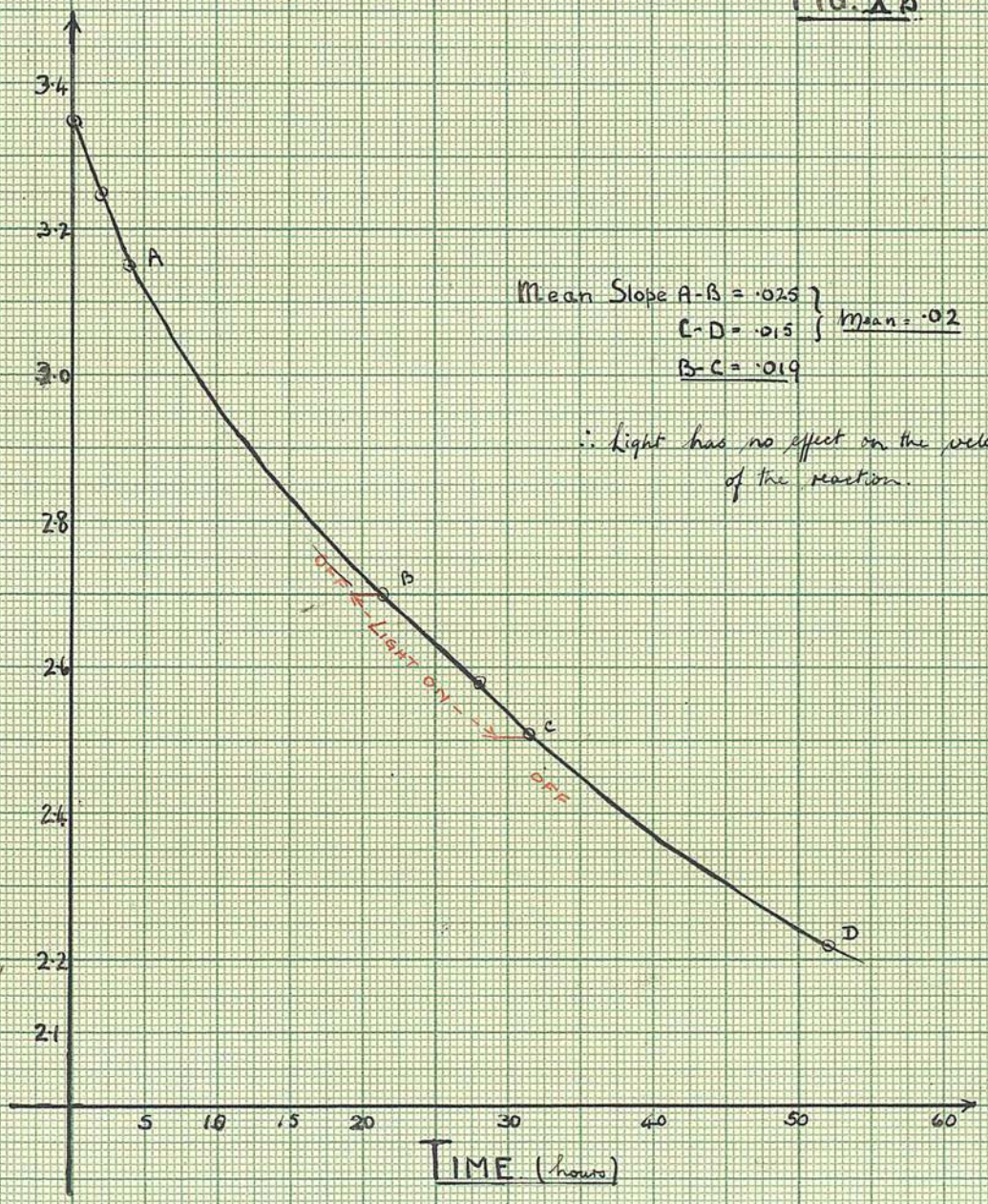


FIG. X.

The bulb was heated to 10°C above the temperature of the thermostat for one day. It was then cooled to 30°C and readings of pressure taken at regular intervals of time. The bulb was illuminated during one period of the reaction but as the graph (Fig. X b)

FIG. X b.



Mean Slope A-B = ·025
C-D = ·015
B-C = ·019
Mean = ·02

∴ Light has no effect on the velocity of the reaction.

shows no photochemical effect was observed.

Evidence for the existence of the molecule C_2H_4I.

The existence of such a molecule as C_2H_4I receives some support from the work of Berthoud[25] The photochemical bromination of cinnamic acid or of stilbene (which is similar) follows the same scheme:-

1) $Br_2 + h\nu \rightarrow Br + Br$

2) $A + Br \rightarrow A\,Br$

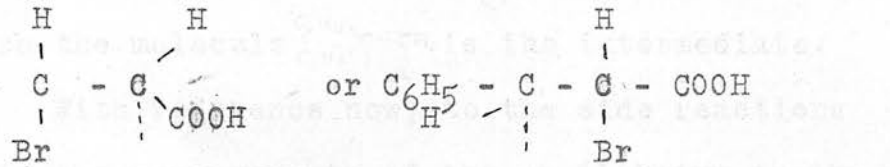
3) $A\,Br + Br_2 \rightarrow A\,Br_2 + Br$

(etc. as a chain)

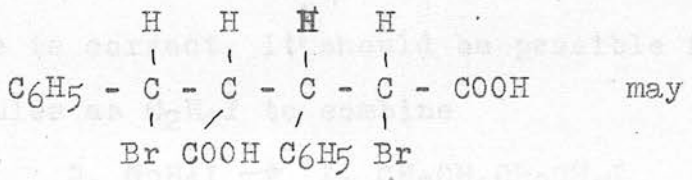
4) $2\,Br \rightarrow Br_2$

5) $A\,Br + Br \rightarrow A\,Br_2$

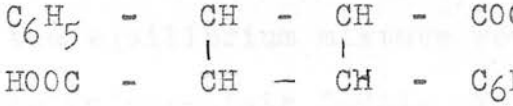
For the case of cinnamic acid, ABr has the structure.



If two of these molecules combine the resultant molecule



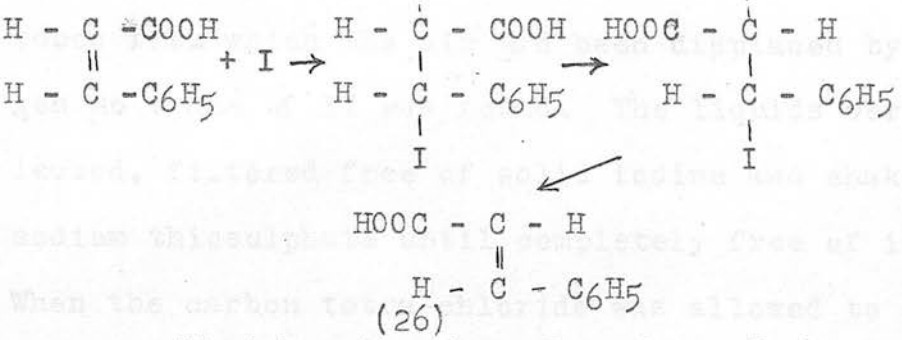
may lose bromine and give α-truxillic acid which has the structure :-



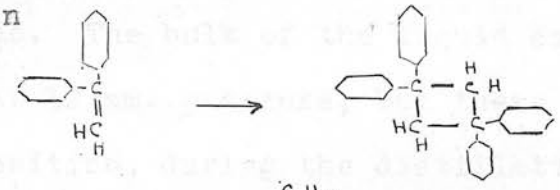
It may be remarked here that truxillic acid is actually formed when solid cinnamic acid is illuminated with ultra violet light.

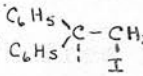
The isomerisation of allo-cinnamic acid[25] in presence of iodine is a further proof of the

existance of this type of intermediate. The scheme given by Berthoud is the following.



Hildebrand[a] has also shown that asym. diphenyl ethylene polymerises readily in presence of iodine to give a dimeride. This may be a similar type of reaction



in which the molecule  is the intermediate.

With reference now, to the side reactions found in the measurements of the equilibrium in the decomposition of ethylene diiodide, if Schumacher's scheme is correct, it should be possible for two such molecules as C_2H_4I to combine

2. $C_2H_4I \rightarrow I.CH_2CH_2CH_2CH_2I$

to give di-iodo-butane. The existence of such a compound in the equilibrium mixture would prove the presence of the intermediate C_2H_4I. To test this, some thick glass bombs were partially filled with solid ethylene di-iodide (5 gms in each bomb); the solid was covered with a carbon tetrachloride solution of iodine, and the tubes sealed off. After being kept

in an oil thermostat at 130°-140°C. for three weeks they were cooled and opened. Those which had contained an air space smelt strongly of HI but in those tubes from which the air had been displaced by nitrogen no trace of HI was found. The liquids were collected, filtered free of solid iodine and shaken with sodium thiosulphate until completely free of iodine. When the carbon tetra-chloride was allowed to evaporate off, a heavy brown oil which had a strong terpene smell remained. The oil (about 1 gram in all) was shaken with water, centrifuged, dried and distilled in vacuo. The bulk of the liquid came over at 90°-100°C at 12 mm. pressure, but there was a good deal of decomposition, during the distillation and the distillate was coloured with free iodine.

Di-iodo-butane is solid at 6°C and an amber coloured liquid which boils at 128°C at 18 mm. Hg [27] With piperidine [28] it forms N. tetramethylene piperidinium iodide, a solid of MP 178-180°C.

An unsuccessful attempt was made to obtain this derivative from the oil obtained above. However there is little doubt that the oil originally contained combined iodine and it was probably largely decomposed during distillation. Moreover, the oil obtained was probably not a single compound but a mixture of homologues formed in all probability from C_2H_4I.

2. Ethylene and Bromine.

The reaction between ethylene and iodine has no analogy with the reactions between ethylene and the other halogens, for in the case of bromine and chlorine there is no reverse reaction, the products being stable compounds.

Davis (29) has found that the reaction between ethylene and bromine in solution follows the course of a simple bimolecular reaction.

$$+d\frac{[C_2H_4\,Br_2]}{dt} = k\,[C_2H_4]\,[Br_2]$$

$$\left\{ Cf \; + \; d\frac{[C_2H_4I_2]}{dt} = k'\,[C_2H_4][I_2]^{3/2} \right\}$$

The rate of the reaction is accelerated by the presence of water, but the most interesting feature of the reaction is that is has a negative temperature coefficient. At 0°C the reaction is actually 20-130 times faster than it is at 25°C. Davis explains that the reaction requires the formation of a bromine hydrate Br_2H_2O. The equilibrium for this hydrate is displaced towards formation with lowering of temperature. The only known hydrate of bromine is either Br_2 10 H_2O or $Br_2 8H_2O$, (30) which crystallises out at 3°C and decomposes at 6.8°C at atmospheric pressure. One would expect therefore that if such a hydrate were involved, sufficient changes in its concentration would occur at these temperatures to produce a noticable change in the acceleration of the reaction as the temperature is lowered. David however finds that the

rate of the reaction $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$ increases continuously as the temperature is lowered from 25°-0°. Finally, David adduces as evidence for the existence of a bromine hydrate of the formula Br_2H_2O the theory that the Budde effect in moist bromine is due to the existence of such a hydrate. This theory however is now discredited. It is therefore rather unlikely that a hydrate of bromine plays any considerable part in this reaction.

Other reactions which have a negative temperature coefficient are known, but these are termolecular reactions. The reaction

$$2NO + O2 \rightarrow 2NO_2$$

which proceeds according to the kinetic equation.

$$+\frac{d[NO_2]}{dt} = k[2NO]^2[O_2]$$

is actually $3\frac{1}{2}$ times faster at 0°C than at 389°C. The explanation of this is that a triple collision is necessary for reaction to take place. The temperature coefficient kt +10/kt varies from .912 to .997 as the temperature rises. This indicates that a very low heat of activation is to be expected. If, however the reaction requires any heat of activation at all, it means that the temperature coefficient should be just above unity. The depression of the coefficient to .91 is due to the decreasing chance of a ternary collision as the temperature rises. The period of time during which two molecules are in collision decreases with rising temperature and therefore the chance of a third molecular impact during this time is decreased.

This can hardly be the explanation of the reaction between C_2H_4 + Br_2 in carbon tetrachloride solution, because, even if triple collisions are required, something more must be necessary since Norrish has found that in the gas phase, if the walls of the reaction vessel are coated with paraffin wax, there is no reaction between ethylene and bromine. Yet the pressures of the gases are in the neighbourhood of atmospheric pressure so that triple collisions frequently occur. (1 in 10^3-10^4 collisions are triple collisions.)

The above experiment of Norrish shows that there is no appreciable homogeneous reaction in the gas phase; it is therefore not unreasonable to assume that the reaction in solution is largely or completely a surface reaction. The similarity in the kinetics of the two reactions support this idea. This would account both for the accelerating influence of water and the negative temperature coefficient. If the reaction takes place on a layer of bromine adsorbed on the glass surface, a rise in temperature might retard the reaction since at the higher temperature less bromine will be adsorbed on the glass surface.

Some work has been done which shows that not only is there a heterogeneous reaction between ethylene and bromine in solution, but the reactions between ethylene and chlorine and ethylene and iodine can also take place on a glass surface.

3) Experimental.

Solutions (about N/100) of chlorine, bromine, and iodine were made up in pure carbon tetrachloride and standardised by titration with standard N/100 thio sulphate. A solution of ethylene in carbon tetrachloride was also prepared. For the experiment two stoppered 250 ccs. bottles of equal dimensions were employed. The internal surface area measured approximately 120 sq. cms. Bottle I. was nearly filled with glass beads to give a large surface area, Bottle II contained no glass beads. 50 ccs. of ethylene solution and 50 ccs. halogen solution were mixed in each bottle. The bottles were then kept in a thermostat and in the dark. Readings of the halogen content were made at regular intervals by withdrawing portions of 10ccs. and titrating with $\frac{N}{100}$ thiosulphate. The results are given in tables VI, VII, VIII, and in Figs. XI. XII. XIII. In all cases the temperature was 11°C.

TABLE VI.

Ethylene and Chlorine.

Time Minutes	ccs N/100 Na thiosulphate	
	Bottle I.	Bottle II.
-	6.07	6.07
14	4.30	
17		5.37
53	3.49	
56		5.21
111	2.55	
117		5.07
248	1.20	
252		4.93

FIG. XI

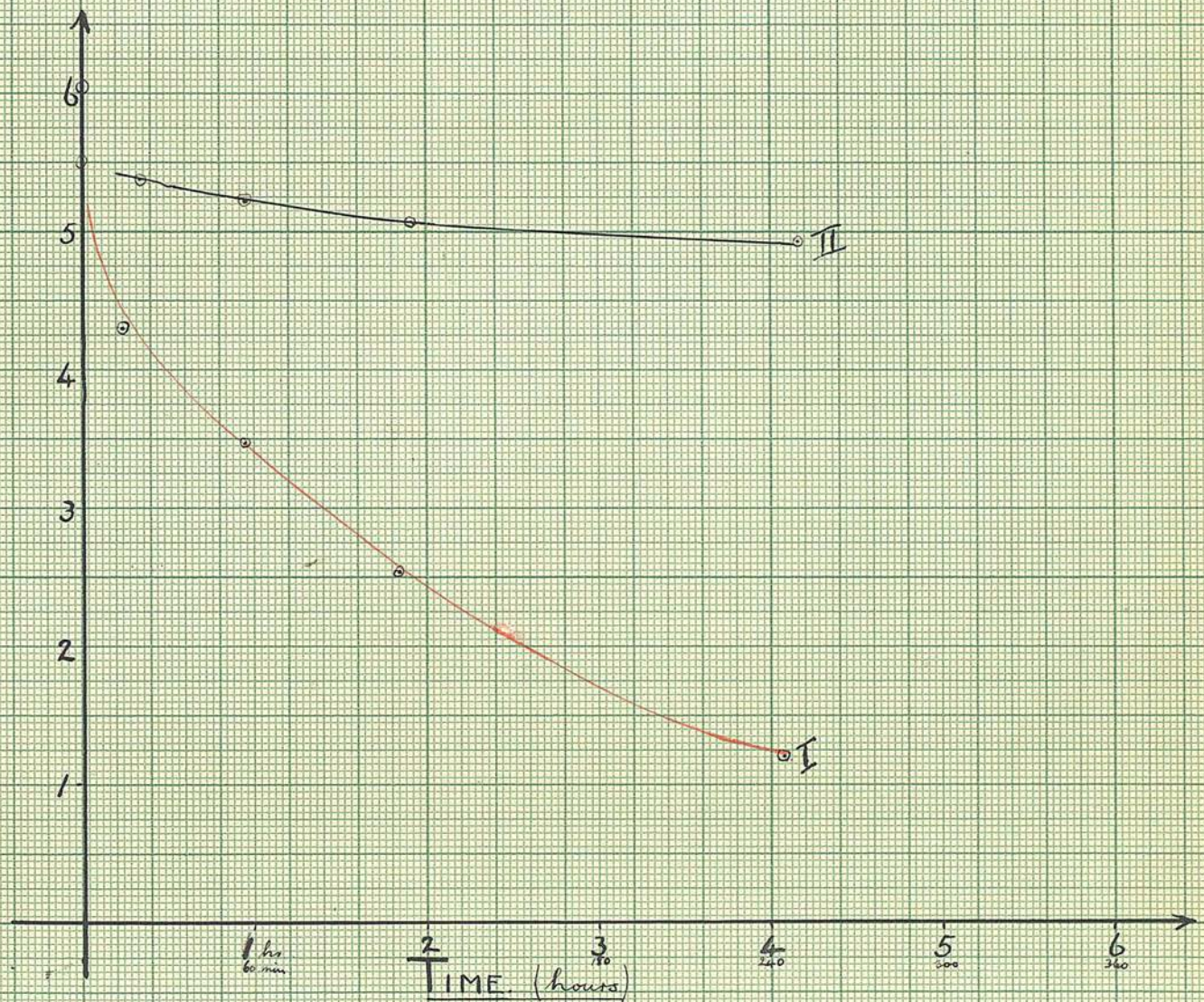


FIG. XII

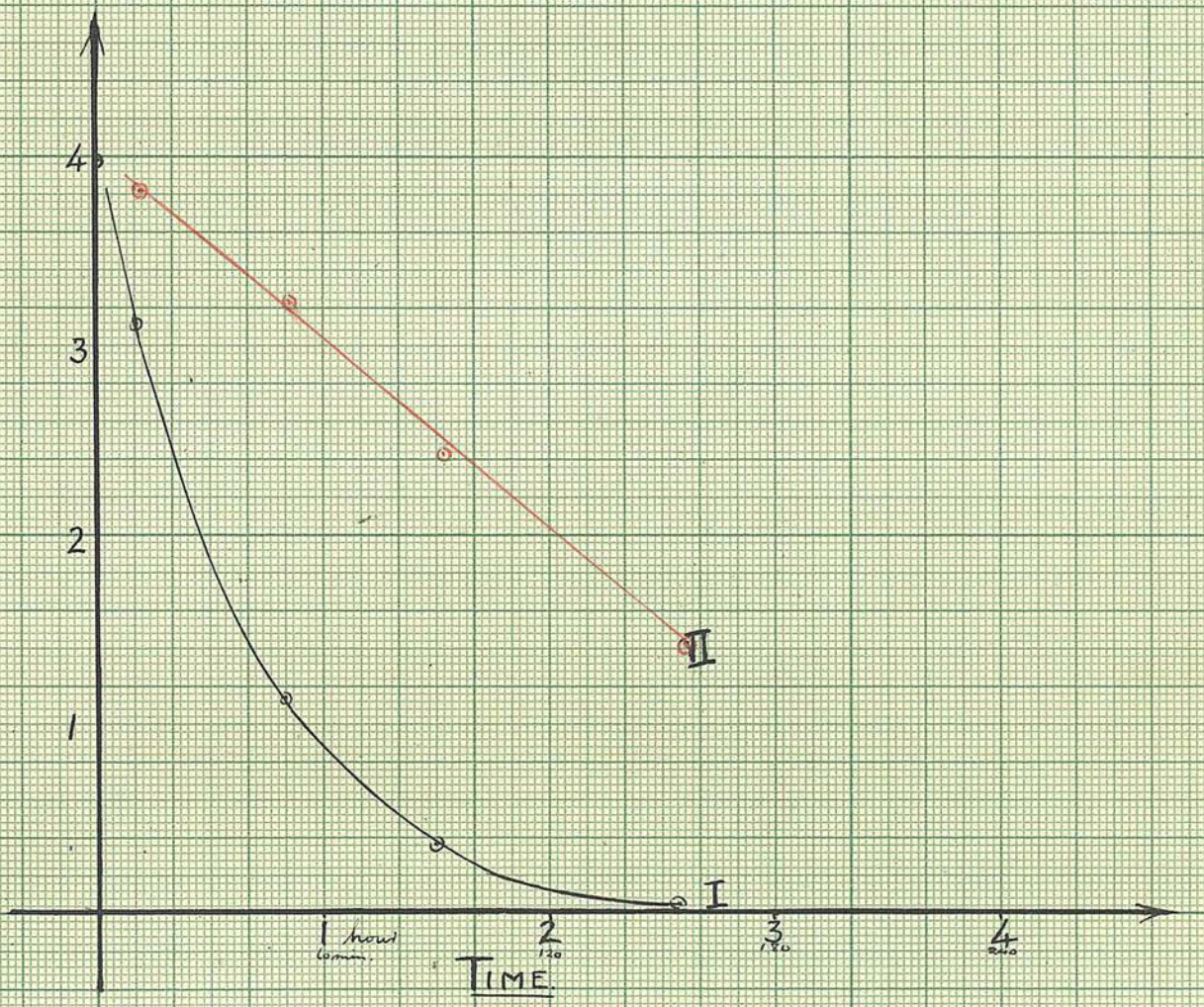


FIG. XIII

TABLE VII.

Ethylene and bromine.

Time Minutes	ccs N/100 Na thiosulphate	
	Bottle I,	Bottle II.
-	3.98	3.98
10	3.12	
12		3.82
50	1.15	
52		3.25
90	.37	
92		2.43
155	.06	
157		1.44

TABLE VIII.

Ethylene and Iodine.

Time Hours	ccs n/100 thio-sulphate	
	Bottle I.	Bottle II.
-	7.47	7.47
.5	7.36	
18.67	7.27	7.43
45.15	7.12	
93.1	7.04	7.44
169.5	6.80	7.47

The results show that the reaction between Br_2 and C_2H_4 and Cl_2 and C_2H_4 in $C Cl_4$ solution are surface reactions taking place on an adsorbed layer on glass surface. This is exactly the same reaction as the reaction studied by Norrish etc. and Stewart etc. for the gaseous reactants. The effect of moisture, and the negative temp. coefficient of the Br_2-C_2H_4 reaction easily fall into line with this suggestion.

In the case of iodine again there is good agreement with the gas reaction. There is a very slight reaction on the glass surface but this reaction is negligible compared with the Br_2 and Cl_2 reaction. It will be remembered that the reaction between I_2 and C_2H_4 on glass surface was found to be very slow for the gases.

At higher temperatures the homogeneous reaction between I_2 and C_2H_4 becomes much more important than the surface reaction; there is however evidence from Polissar's results for a slow decomposition of $C_2H_4I_2$ not catalysed by I atoms. This is in all probability a slow decomposition of $C_2H_4I_2$ on the glass surface corresponding to the slow formation shown in Table VIII. and Fig. XIII.

PART II.

APPARATUS.

The Hydrogen Tube.

It is well known that if a discharge is passed through hydrogen at low pressures a discontinuous spectrum consisting of the Lyman, Balmer and Paschen line series is obtained. If however the pressure is increased to pressures of the order 1-2 m.m. the spectrum becomes perfectly continuous in the ultra violet. Such a discharge is more convenient than an under water spark; the spectrum stretches further into the ultra-violet. Moreover the tube is perfectly silent in use.

The construction of the tube finally used, is shown in diagram Fig. XIV. A silica tube A with glass connecting pieces fitted and waxed over the side tubes at b and b^1 forms the discharge tube Taps T and T^1 are used for adjusting the hydrogen pressure. Copper wires were sealed into the tube at B and B^1. The aluminium electrodes were fixed at e and e^1, the one at e^1 being hollow so that the radiation could pass through to the quartz window W which was fixed with picein. The whole tube was cooled by running water. J is a series of jets which played on the hottest and on the waxed portions of the tube so that the temperature of the water in the brass tank never rose above 15°C.

Other tubes were tried which had the electrodes contained in side tubes at right angles to the discharge.

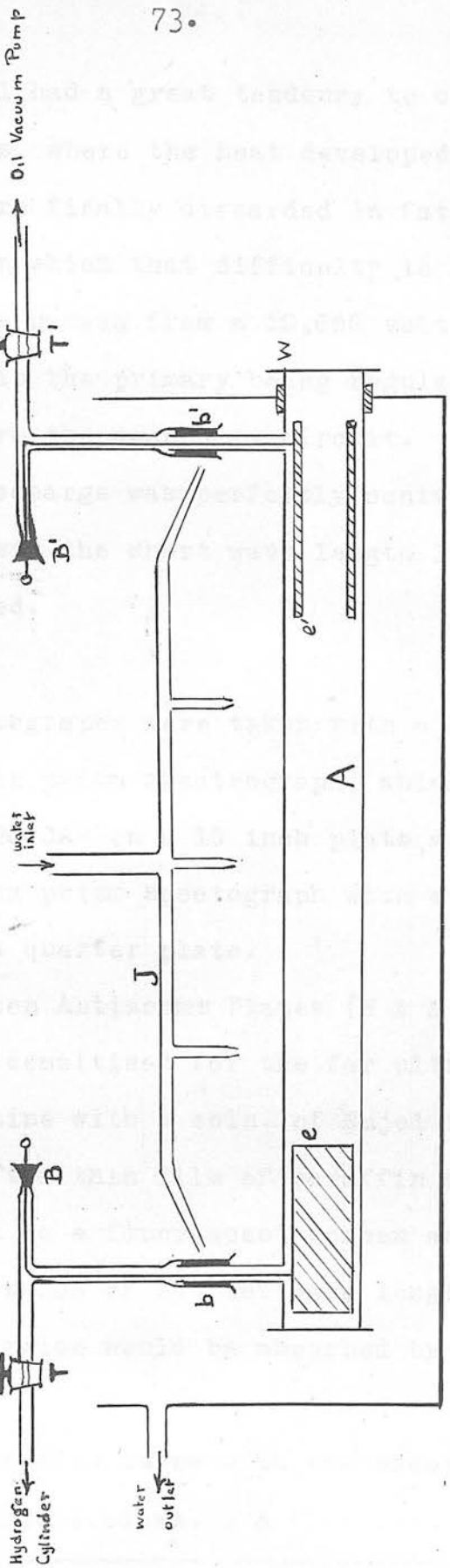

0.1 Vacuum Pump
T'
W
b'
B'
e'
A
water inlet
J
B
e
b
T
Hydrogen Cylinder
water outlet

FIG. XIV

tube but they all had a great tendency to crack at the right angle bends, where the heat developed was very great. They were finally discarded in favour of the one described, in which that difficulty is removed. The discharge was passed from a 10,000 volt transformer, the current in the primary being regulated so that .5 amp passed thro the secondary circuit. The light given by this discharge was perfectly continuous up to 1,800 A°* which was the short wave length limit of the spectroscopes used.

The photographs were taken with a Bellingham and Stanley quartz prism spectrograph, which had a range of 8000A°-2000A° on a 10 inch plate, and with a small Hilger quartz prism spectograph with a range of 8000A°-1800A° on a quarter plate.

Wellington Antiscreen Plates (H & D 450) were used., They were sensitised for the far ultraviolet by coating the gelatine with a soln. of Nujol in petrol ether. This left a thin film of paraffin on the plate, which acts as a fluorescent screen and brings out the lines or bands of shorter wave length than 2300A° which otherwise would be absorbed by the gelatine.

The absorption tubes with one exception were of quartz with plane windows. A five foot glass tube

---

*The continuity of the hydrogen tube is broken by oxygen absorption bands. (See Plate III.)

fitted with quartz windows was used for cyanogen.

If an absorption tube required to be heated during the photograph it was done in the following way. It was wound with stout copper wire so that $\frac{3}{4}$" of the winding protruded over each end of the tube. This was covered with a thin layer of asbestos paper on which the heating resistance wire was wound. This was covered by a further layer of asbestos paper and a winding of asbestos string.

By having the heating coil extending over the end of the tube, the windows were kept at the same temperature as the tube which prevented condensation of solid or liquid on their surface. The tubes which did not require to be heated in the manner described, had a side tube into which the contents could be frozen by liquid air.

The method of photographing the absorption of each gas was to expose for 2-4 hours with the gas at a known pressure,* remove the gas by cooling with liquid air, if necessary, and expose for an equal time to obtain a blank. A copper zinc spark was added to each plate for register lines. By using a Hartmann diaphragm which uncovers only a portion of the slit for each exposure the position of the plate remained unaltered for the photographing of these register lines

---

*The vapour pressure of Cyanogen Iodide is not known, but from the analogy of Cl_2-CNCl and Br_2-CNBr it is probable that the vapour pressure of CNI at Room temperature is slightly less than the vapour pressure of iodine.

and thus the photographs were accurately comparable.

Materials. The method of preparation of the cyanogen halides has been described in a previous section.

Cyanogen was prepared as before by heating Mercuric cyanide, but in this case the gas was carefully purified by fractional distillation. Only the middle fraction of the liquid cyanogen was used.

Results.

Cyanogen Chloride. (cyanogen impurity.)

The absorption spectrum of cyanogen chloride at 15°C and atmospheric pressure, in a quartz tube 25cm long, is shown in Plate I. The absorption is continuous, the long wave length limit is about2240A° which is equivalent to 127 kcal. The photograph also shows a few bands about 2190 A° which are due to cyanogen (see p.82)

Cyanogen Bromide. Plate II. shows the absorption spectrum of CNBr. The temperature of the tube (25cm) was 15°C which corresponds to a vap. press. of CNBr. The absorption is again continuous the long wave length limit in this case being at 2540A° (=112 kcal.)

Cyanogen Iodide. Plate III. has two regions of continuous absorption. At 3100A° (92 kcal) absorption begins and reaches a maximum at 2500A°. The second region begins about 2150A° (132 kcal.)

Cyanogen. The absorption spectrum of cyanogen was photographed for pressures of cyanogen varying from

Plate I.

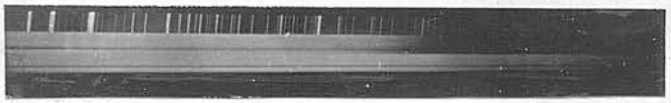


Plate II.

Plate III.

Plate IV.

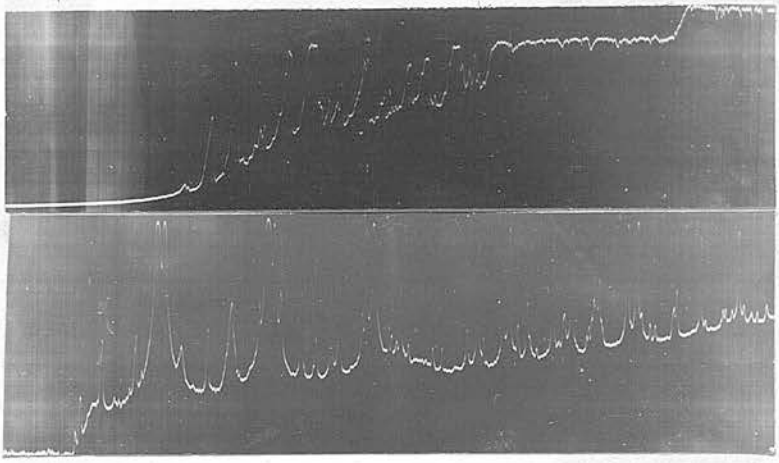


Plate V. (a) and (b).

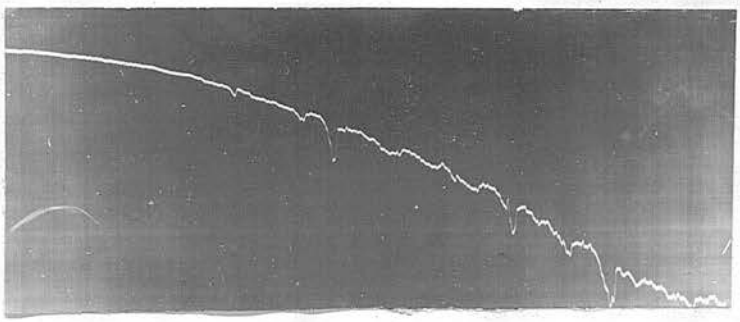


Plate VI.(a)

Plate V.

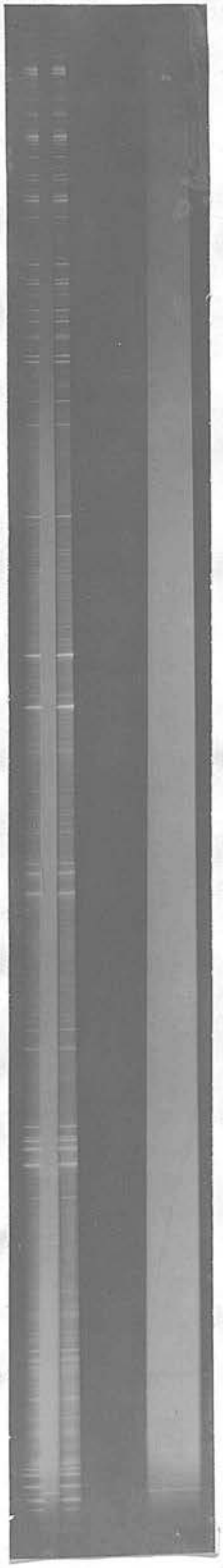


Plate VI.

23mm to 760mm and at a temperature of 15°C. Plates IV. V. and VI. with their photometric registers show that in this case the absorption is not continuous, but consists of a series of more than forty bands beginning about λ = 2500A° and extending to, λ = 2040A°. By far the greater number of the bands occur in the region λ =2250A° - λ =2040A°. The bands have been measured and registered on a photometer but since plate V. shows the bands most clearly it alone will be described in detail. The bands are shaded towards the red, showing that in the excited state the molecular linkage is weaker than in the normal state. Some of the bands, notably 3, 8, 12 (see table IX) show a good deal of rotation structure.

Calibration of Plate V. The distance (d) from a fixed point on the plate, of a number of standard lines in the Copper zinc spark was measured. From any two of these lines a dispersion formula of the general form,

$$d = A + B/\lambda^2$$ can be derived.

This formula shows a linear relationship between d and $1/\lambda^2$ but if the graph d - $1/\lambda^2$ is plotted for a number of lines it is found to deviate slightly from the straight line. By noting this deviation at various points on the curve, a second graph can be drawn plotting deviation against d. This error curve, together with the dispersion formula furnish the all the data necessary to calculate an accurate value of λ from d.

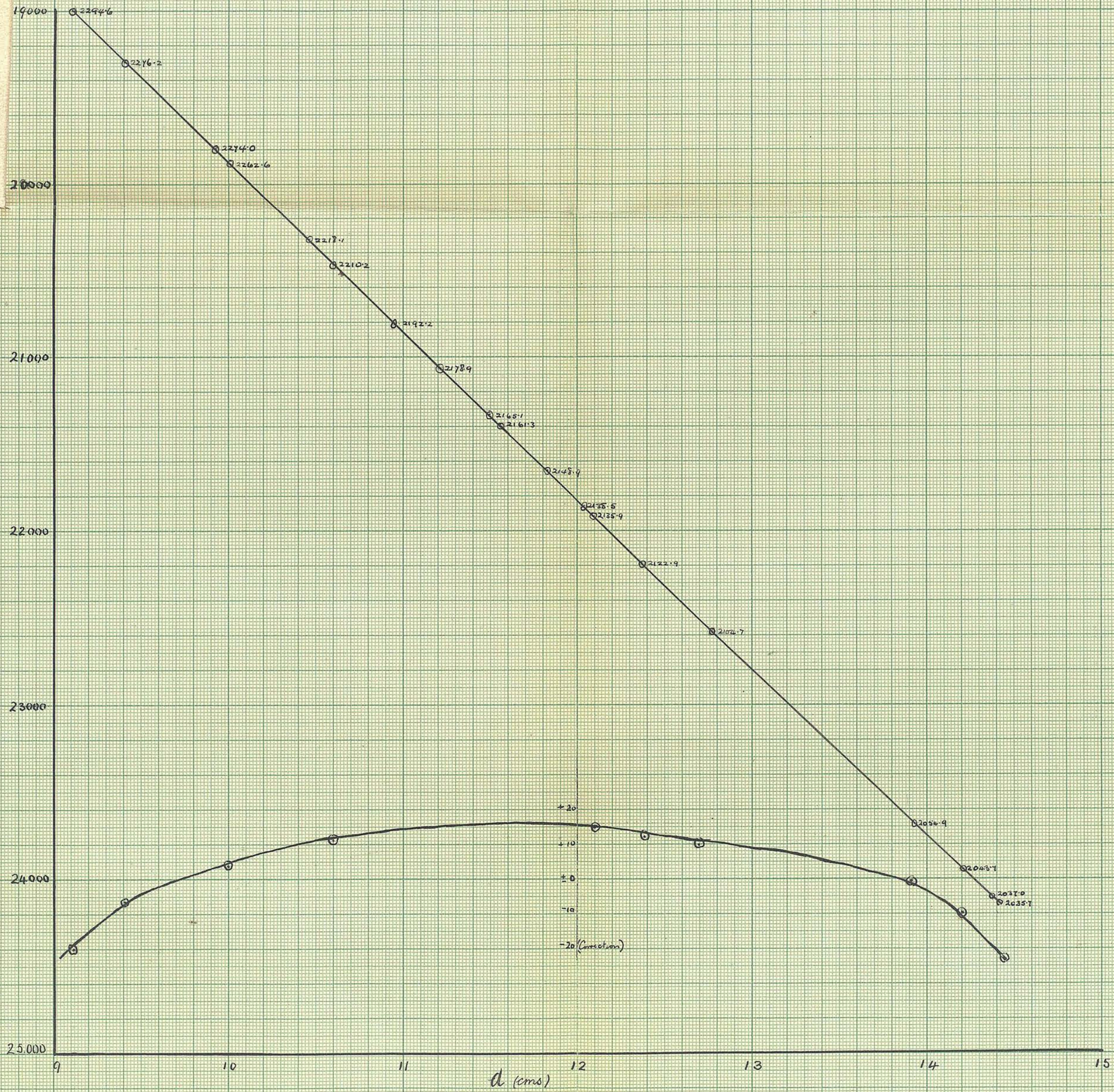

19000
20000
21000
22000
23000
24000
25.000
22946
2296·2
2274·0
2262·6
2218·1
2210·2
2192·2
2178·9
2165·1
2161·3
2148·9
2138·5
2135·9
2122·9
2102·7
2054·9
2043·7
2037·0
2035·7
+20
+10
±0
-10
-20 (Correction)
9
10
11
12
13
14
15
d (cms)

FIG XV

The interpolation formula was calculated from the copper lines λ = 2247.0A° (d=9.92) and λ =2054.9A° (N=13.924) thus

$$d = A + B/\lambda^2$$

$$9.92 = A + B \times 19806.0$$
$$13.924 = A + B \times 23682.5$$
$$\therefore \quad 4.004 = B \times 3876.5$$

Hence $B = 1.03289 \times 10^{-3}$
and $A = -10.537$

From which the value for $1/\lambda$ may be derived.

$$1/\lambda = \left(\frac{d + 10.537}{1.03289 \times 10^{-3}}\right)^{\frac{1}{2}}$$

Table IX. gives a number of these standard lines with corresponding values of d and e, the error in the dispersion formula.

TABLE IX. Standard Lines.

Wave length	d mm.	$1/\lambda$ true	$1/\lambda$ calcd.	Correction e.
2369.9	7.904	42195.9	42253.7	-57.8
2294.4	9.101	43584.4	43603.5	-19.1
2276.2	9.405	43932.9	43939.7	- 6.8
2247.0	9.920	44504.0	44503.5	+ 0.5
2242.6	9.997	44591.1	44586.6	+ 4.5
2218.1	10.446	45083.6	45072.0	+11.6
2210.2	10.596	45244.8	45232.8	+12.0
2192.2	10.944	45616.3	45603.7	+12.6
2178.9	11.198	45894.7	45872.5	+22.2
2165.1	11.486	46187.2	46.75.4	+11.8
2161.3	11.561	46268.4	46254.0	+14.4
2148.9	11.818	46535.2	46525.8	+ 9.4
2138.5	12.036	46761.7	46748.5	+13.2
2135.0	12.089	46818.7	46803.3	+15.4
2126.0	12.301	47036.7	47028.3	+ 8.4
2122.9	12.370	47105.4	47093.1	+12.3
2104.7	12.770	47512.7	47502.5	+10.2
2054.9	13.924	48664.6	48664.3	+ 0.3
2043.7	14.202	48930.6	48940.0	- 9.4
2037.0	14.370	49091.6	49105.9	-14.3
2035.7	14.410	49122.2	49145.3	-23.1

Fig. XV. shows the graph of d. plotted against $1/\lambda^2$ from the results in columns (2) and (3) in table and the error curve plotted from results in columns (2) and (5) In Table X. the absorption bands of

cyanogen are given with the corresponding calculated values of $1/\lambda$. The intensities (column 4) are obtained from the photometer curve (Plate Va.)

TABLE X.
Absorption Bands of $(CN)_2$

Band No.	d.+ 10.537	$1/\lambda$ calcd.	$1/\lambda$ corrected	Intensity.
15a	20.373	44412.0	44412.0	
b	.399	44440.3	44440.3	0
14	.621	44681.5	44685.5	
	.742	44812.4	44818.4	1
	.769	44841.5	44848.0	
13	.825	44902.0	44909.3	3
12e	.901	44988.1	44996.4	
d	.962	45049.4	45058.6	
c	21.007	45098.2	45108.0	
b	.053	45147.1	45157.3	
a	.092	45188.9	45199.7	1
	.168	45270.2	45281.4	
	.221	45326.9	45338.6	
	.265	45373.8	45385.6	
11	.323	45435.7	45448.1	
	.385	45501.7	45514.5	6
	.436	45555.9	45568.9	
10	.561	45583.5	45596.5	
a	.595	45724.6	45738.1	
b	.621	45752.1	45765.8	10
a1	.652	45784.9	45798.7	
b1	.677	45810.8	45824.7	
	.731	45868.3	45882.2	
	.751	45889.4	45903.3	1
9	.792	45932.6	45946.6	2
8d	.937	46085.2	46099.2	
c	.971	46120.9	46134.9	
b	.999	46150.3	46164.3	3
a	22.027	46179.6	46193.6	
7d	.084	46239.3	46253.5	
c	.112	46268.7	46282.9	1
b	.148	46306.4	46320.6	
a	.176	46335.6	46349.6	
7[1]a	22.232	46394.0	46408.1	
b	.252	46418.0	46432.1	
c	.287	46451.4	46465.5	
d	.322	46487.8	45601.8	
6	.423	46592.8	46606.8	3
5	.543	46717.4	46731.2	4
41	.643	46820.9	46834.5	
4	.860	47044.7	47057.1	10

TABLE X. contd.

Band No.	d.+ 10.537	$1/\lambda$ calcd.	$1/\lambda$ corrected	Inten-sity
3	22.955	47091.0	47103.3	)
	.962	47149.6	47161.6	(5
	23.004	47192.7	47204.4	)
	.046	47235.7	47241.0	(
0	24.057	48260.7	48264.7	10

Discussion of Results. The absorption spectra of such gases as the halogens consists of a series of bands which converge, as the frequency increases, to a head through which the absorption passes into a region of continuous absorption. Franck (31) has given an interpretation of these spectra. The bands correspond to a quantised absorption of light which increases the electronic energy of the molecule. This alters the vibration and weakens the binding forces of the molecule. At the point of convergence the absorbed energy $h\nu_c$ is just sufficient to overcome these binding forces and the molecule is dissociated. The energy represented by this $h\nu_c$ limit is, in the case of halogens, greater than the Heat of Dissociation calculated from thermal data. Thus Franck has shown that photodissociation has resulted not in the production of two atoms, but of one atom in the normal state and one carrying an excess or excitation energy E. The process of photo dissociation therefore takes the following course:-

The molecule absorbs a quantum $h\nu$

If $h\nu$ is less than $h\nu_c$ (the convergence limit) the

molecule is activated (Stern and Volmer) and in a state to act chemically with another molecule should it collide with one during its period of excitation. If no collisions occurs during this time (at low pressures this is possible) the molecule re-emits its excitation energy as a fluorescence radiation.

If $h\nu$ is greater than $h\nu_c$ the molecule will dissociate into a normal and an excited atom, carrying sufficient kinetic energy to make up the difference $h\nu - h\nu_c$. Since the K.E. may have any value, the energy absorbed $h\nu$ will not be subject to any quantum restriction and the spectrum will be continuous.

This explanation holds equally for the dissociation of a heteropolar molecule like NaCl, where there are no bands in the absorption. The region at which continuous absorption begins (ν_c) indicates the energy ($h\nu_c$) necessary to dissociate the molecule, in this case into unexcited atoms)

The value $h\nu_c$ can of course only be measured accurately if the absorption of the gas covers this region. It may happen that the maximum absorption occurs as in the case of chlorine well beyond the convergence limit. If it falls off completely on the short wave length side of $h\nu_c$ the observed absorption limit $h\nu$ will be represented by

$$h\nu = D + E + K.E. \quad \ldots\ldots\ldots 1)$$

at ν_c K.E. = 0

$$\therefore h\nu_c = D + E \quad \ldots\ldots\ldots 2)$$

In such a case only an upper limit for D could be found from this formula.

Cyanogen Halides. The decomposition of the cyanogen halides by the continuous absorption of light of wave length shorter than λ_c results therefore in the production of two dissociated parts of the molecule either of which may have, in addition to its dissociation energy, a certain excitation energy represented by:-

$$CN\ X + h\nu_c \rightarrow CN + X^1$$
$$\searrow$$
$$\text{or } X + CN^1$$

These energies of excitation for each of the halogens (32) are

$Cl^1 = 2.3$ kcal $= 0.1$v
$Br^1 = 10.2$kcal.$= 0.45$v
$I^1 = 21.6$kcal.$= .940$

Mulliken has shown from an examination of the red and violet groups of bands of the CN molecule that the CN group has two electonic levels 1.8 volts, 3.2 volts above the normal level.

$CN^1 = 1.81$ volts (41.5 kcal)
$CN^{11} = 3.2$ volts (73.4 kcal)

From equation 2) we can write

$$h\nu_c = D_{CNX} + E_X \text{ or } CN \cdot \quad \ldots\ldots .4)$$

From equation 4) the heat of dissociation can be calculated for the three compounds in the following way

CNCl. $h\nu_c = 127$ kcal

$\therefore D_{CNCl} = 127 - 2.3 = 123.7$ kcal.
$-41.5 = 85.5$
$-73.4 = 53.6$

CN Br. $h\nu_c = 112$ kcal

$\therefore D_{CNBr} = 112 - 10.2 = 111.8$ kcal.
$- 41.5 = 70.5$
$-73.4 = 38.6$

CNI 1), $h\nu_c$ = 92 kcal

$\therefore D_{CNI}$ = 92 - 21.6 = 70.4 kcal.
- 41.5 = 50.5
- 73.5 = 18.6

2) $h\nu_c$ = 132 kcal

$\therefore D_{CNI}$ = 132 - 21.6 = 110.4 kcal.
- 41.5 = 90.5
- 73.5 = 58.6

D, in these cases, it must be emphasised is a maximum, for there is no evidence that the absorption region begins exactly at ν_c. The observed $h\nu_c$ may be augmented by kinetic energy as in equation 1). Further, even when KE = 0, $h\nu_{obser.}$ may include vibration energy of the CN molecule which is split off. In table XI. the values obtained for D are compared with the heats of linkage given by Eucken (33) for the bonds C-Cl, C-Br, C-I. An examination of these values shows that the most probable mechanism is, that decomposition results in the formation of a normal halogen atom and an excited CN group. The energy of exitation of the CN group is 41.5 in all cases except for the far ultra-violet absorption of CNI when CN^1 rises to a higher excitation level of 73.4 cal.

TABLE XI.

COM-pound.	Absorption Limit λ_c	kcal	Excitation Energy kcal.	Heat of Dissociation D. kcal.	D calcd. (from Eucken) kcal.
CNCl	2240	127	41.5	123.7 85.5 53.6	73
CNBr	2540	127	41.5	111.8 70.5 38.6	.59
CNIa)	3100	92	41.5	70.4 50.5 18.6	44
b	2150	132	73.4	110.4 90.5 58.6	44

The values given by Eucken represent the mean values of the heats of linkage obtained from the heats of combustion of a series of aliphatic chlorides bromides and iodides.

The heat of sublimation of carbon therefore comes into the calculation. This value cannot be regarded as very certain. Moreover, the C-Cl bond in cyanogen chloride need not be exactly the same as the C-Cl linkage in an aliphatic compound with a longer carbon chain. The first member of a homologous series is often exceptional. For example in methane the heat of linkage of C-H is greater than in the other paraffins. It alone, is not attacked by atomic hydrogen to give CH_3 and H_2. The other paraffins are all decomposed thus $R\,CH_3 + H \rightarrow R\,CH_2 + H_2$. It is therefore possible that the C-Cl linkage is greater in CNCl than in say, C_2H_5Cl. In spite of this source of error however, it is probable that the values obtained from the absorption spectra are too high, due to the fact that the absorption of the gas does not begin at ν_c.

The mechanism of the decomposition of the cyanogen halides by light may therefore be written

$$CNCl + h\nu_{CNCl} \rightarrow CN^{1} + Cl$$
$$CNBr + h\nu_{CNBr} \rightarrow CN^{1} + Br$$
$$CNI + h\nu_{1} \rightarrow CN^{1} + I$$
$$CNI + h\nu_{2} \rightarrow CN^{11} + I$$

(where CN^{1} has excitation energy = 41.5 kcal and CN^{11} has 73.4 kcal)

These figures lend no support to the results of Zappi and Elorza (34) who find from chemical data that in solution, CNCl has the structure of an iso-nitrile

Cl-N=C, CN Br is an equilibrium mixture of the nitrile and iso-nitrile while CNI is a true nitrile. If cyanogen chloride had the structure Cl-N=C, the energy necessary to break the N-Cl linkage, although not definitely known can be calculated from the heat of formation of nitrogen tri-chloride.

$$\begin{aligned} 1/2\ N_2 + 3/2\ Cl_2 &= NCl_3 - 54.7 \text{ kcal.} \\ 1/2\ N_2 &= N - 105 \text{ kcal.} \\ 3/2\ Cl_2 &= 3Cl - 85 \text{ kcal.} \end{aligned}$$

$$\therefore N + 3Cl = NCl_3 + 105 + 85 - 54.7 = NCl_3 + 135.3$$

$$\therefore \text{N-Cl linkage must be} \simeq \frac{135.3}{3} = 45 \text{ kcal.}$$

If it is assumed as before that the CN group is broken off with 41.5 kcal. energy of excitation then absorption would take place at 3300 A°. This absorption region has not been found. It is much more probable if one bears in mind the regular nature of the series of the absorption limits that in the gaseous state the halides of cyanogen have all the same structure namely that represented by the formula X - C ≡ N where X is Cl_1, Br_1 or I.

Cyanogen. The bands have not yet been followed out to the convergence limit and it is therefore not possible to give an accurate value of the heat of dissociation of cyanogen. From the appearance of the band spectrum however it can safely be assumed that the convergence limit lies on the short wave length side of 1850A°. This will give a lower limit for the heat of dissociation of cyanogen. The possible results of this photo

dissociation are :-

$$(CN)_2 + h\nu_c \rightarrow CN + CN_1 \quad 1) \quad \text{or} \rightarrow C_2N + N \quad 5)$$
$$\rightarrow CN + CN^{1} \quad 2) \qquad \rightarrow C_2 + N + N \quad 6)$$
$$\rightarrow CN + CN^{11} \quad 3) \qquad \rightarrow C + C + N + N \quad 7)$$
$$\rightarrow CN + CN^{111} \quad 4)$$

In cases 5)-7) any one of the products may have an additional energy of excitation.

Case 1) can be discarded at once for the reaction $(CN)_2$ CN + CN requires only 71 kcal. and the energy absorbed is 154 kcal at least. The second possibility is also unlikely as it requires only 112 kcal The third reaction requires 145 kcal. and therefore is just possible, but the possibility of there being a still higher but as yet unknown excitation level CN^{111} cannot be neglected and in the absence of any upper limit for $h\nu$ all the other possibilities 5)-7) must also be considered, although they are not so probable as 3) or 4). For instance 7) would require 495 kcal. which would mean (ν_c) = 570A° and 6) requires 424 cal. which corresponds to ν_c = 660A°. Reaction 5) requires 212 kcal. and therefore is not so probable as 3) or 4). If reaction 3) is the true mechanism it leads to a heat of dissociation 82 kcal for the lower limit.

The values for the heats of dissociation calculated in the above discussion were based on the values given by Eucken for the heat of the C-C linkage (71 kcal) and for the heat of the C≡N linkage(212 kcal)

The heat of decomposition of cyanogen to 2(CN) can be calculated from the known values for the

heat of sublimation of carbon (304 kcal), the heat of dissociation of nitrogen (210 kcal) and the heat of dissociation of the CN group (187 ± kcal. from band spectra)[35]

1) $(CN)_2$ = 2C diamond + N_2 + 73.8 kcal(Landolt Bornstein)
2) 2C diamond= 2C gas - 304 kcal.
3) N_2 = 2N - 210 kcal.
4) CN = C + N - 187 ± 10
5) ∴ 2CN = 2C gas + 2N - 374
6) 2CN = $(CN)_2$ + Q
7) ∴ $(CN)_2$ = 2C gas + 2N - 374 - Q

From 1) 2) and 3) $(CN)_2$ = 2C gas + 2N - 514 + 73.9
∴ Q = 440 - 374 = 66 kcal.

This value for Q cannot be regarded as reliable as Eucken's value of 71 kcal. for the C-C linkage. The possibilities of error in Eucken's value have already been discussed. The same sources of error are present in the above calculation but in addition the possible error in equation 4) is 10 kcal. so that Q may be as much as 20 kcal. in error.

The results of this investigation are summarised in Table XII.

TABLE XII.

Substance	Heat of Dissociation Opt.	Heat of Dissoc. calcd.
Cyanogen Chloride	78.5 kcal.	73 kcal
Bromide	70.5	59
Iodide	50.5-58.6	44
Cyanogen	82 kcal	66: 71(Eucken)

PART III.

THE FLAME SPECTRUM OF SULPHUR.

In continuation of the work begun on the flame spectrum of sulphur, suggested by the blue glow surrounding the flame of the Hydrogen chlorine combustion it was quickly established that the blue colour of the flame of sulphur burning in air was due to the same emitter, and that the blue colour was due to the long wave length portion of the band system. This has since been published by Kondratjew (36)

In the flame of sulphur burning in the air, however, there is an additional white light which is continuous and overlaps the S_2 bands, passing into the region of the SO bands. The SO bands have been described by Henri and Wolff (37). It is not yet possible to give any definite explanation of the emission of the continuous spectrum but it may be due to unquantised emission from the chemical combination at high pressure of excited sulphur and oxygen atoms forming SO which is then oxidised to SO_2.

It was thought more desirable to study the spectrum in its simpler form, excited either by the Hydrogen-chlorine flame or the hydrogen-oxygen flame.

The first papers to give an analysis of the spectrum are those of Rosen (38) who worked on both the absorption and fluoresence spectra. Since the enclosed paper was published the analysis has been carried further by Swings (39), Rompe (40) Naudé (41) and Christy and Curtis (42). These workers have mainly confined their

attention to the analysis of the rotational fine structure of the spectrum. In none of these experiments has the flame emission been studied and this spectrum has points of interest of its own.

It has been suggested that the band spectrum produced when sulphur is present in the oxygen hydrogen flame might be a resonance spectrum, because the light emitted from the OH bands which is strongly emitted from the flame should be capable of exciting the fluorescence spectrum, just as light of the same wavelength from the mercury arc can do. An experiment was performed in which the radiation from the oxy.hydrogen flame was thrown upon the same stream of hydrogen carrying H_2S but kept out of contact by a thin wall of silica. No emission of S_2 bands could be found. Although this may have been due to the lack of S_2 molecules in the gas stream, the fact that the hydrogen-chlorine flame, which does not give emission in the region necessary to produce fluorescence, gives the bands, is sufficient evidence that the excitation is due to collision and not to absorption of light.

Another point of interest lies in the fact that the distribution of intensity in the band system appears to be identical as far as inspection can decide whether they are produced in the HCl. or in the H_2O flame. Some differences would probably be observed on the intensity distribution of the rotation lines in the fine structure, but the instruments available are

not suitable for such work.

A further point which has not yet been settled is the occurence of the double headed bands. There is no satisfactory explanation of these. They appear in those bands which arise from a transition from an <u>even</u> level in the excited state and the cause is evidently associated with the excited and not the unexcited molecule. Curtis found that the difference between the frequency of the two heads remains practically constant down into the red region of the spectrum.

The most exact formula representing the sulphur band spectrum is probably that of Naudé and Christy:-

$$V_e = 32250.9 + 429.5\,(v^{1}+\tfrac{1}{2}) - 2.75\,(v^{1}+\tfrac{1}{2})^2 - 727.4(v^{11}+\tfrac{1}{2}) + 2.91\,(v^{11}+\tfrac{1}{2})^2$$

The heat of dissociation calculated from the band spectrum is 4.45 $\pm$ 0.01 volts, in good agreement with the value found by chemical methods (103600 cal= 4.5 volts) The nuclear separation in the lower state is 1.603×10^{-8}cm. and in the upper state it is 1.814×10^{-8}.

Plate VII. is a copy of the photograph taken with a high dispersion glass prism spectrograph. The dispersion is great enough to show the rotation structure. This however is too complex (consisting of 3P and 3R branches) for a satisfactory analysis as the definition is not good.

TABLE XIII.

Frequency of Observed bands		Corresponding Measurements of Rosen	Kondratjew
(v1 N11)	20620	-	-
(3, 19)			
(3, 18)	21300	-	-
(2, 17)	21480	-	-
(3, 17)	21920	-	-
(2, 16)	22080	-	-
(1, 15)	-	22365	22349
(3, 16)	22530	22540	22543
(2, 15)	22750x	22765	22763
(1, 14)		22885	22989
(3, 15)	23220	23188	23175
(2, 14)	23450x	23390	23405
(1, 13)			
(3, 14)	23870	-	23815
(2, 13)	24075x	24039	24050
(3, 13)	24530	-	-
(2, 12)	24710x	24685	24704
(3,12)	25160	25121	-
(2, 11)	25360x	25360	25361
(2, 10)	25950x	-	26028
(2, 9)		26681	26695
(2, 8)		-	27367
(2, 7)		-	28050

x Double Heads with separation = 30 cm^{-1}

TABLE XIIIa.

v^{II} \ v^{I}	2	3	Δ
10	25950		
11	25360		
12	24710	25160	450)
13	24075	24530	455) Mean
14	23450	23870	420) 446
15	22750	23220	470)
16		22530	
17		21920	
18		21300	
19		20620	
Δ	Mean 640	Mean 649	
	Double Heads with separation of about 30 cm^{-1}	Single Heads	

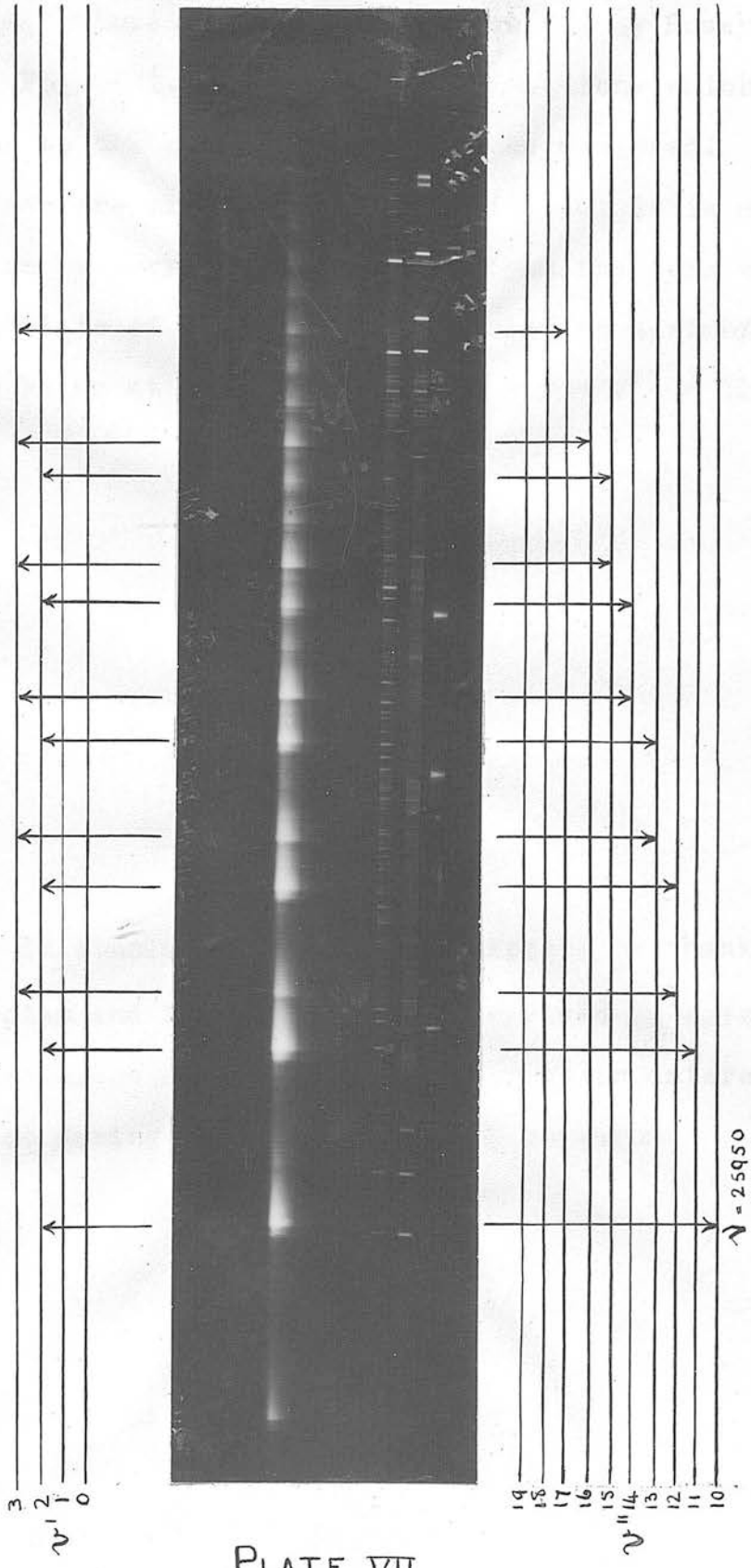


PLATE VII.

FIG. XVI

Table XIII. gives some of the measurements of the heads of the bands. These are compared with corresponding values given by Kondratjew and by Rosen.

Fig. XVI. indicates the transitions which give rise to the bands which have been measured. The quantum numbers are not quite certain, but it is clear that there is very little emission from the zero vibrational state of the excited molecule the maximum emission being at the transition $V^{1} = 2 \rightarrow V^{11} = 10$.

In conclusion, I wish to express my thanks to Dr Ludlam and Dr Mooney, who supervised my work, and to Professor Kendall, F.R.S., for their interest and advice during the course of this research.

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The Hydrogen-Chlorine Flame.

By E. B. Ludlam, M.A., D.Sc., H. G. Reid, and G. S. Soutar.

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Re-inspection of the photograph of the hydrogen-chlorine flame taken in 1924 showed that it likewise exhibited, in addition to some light of longer wave-length, a rapid rise in intensity of emitted light at about λ 480 $\mu\mu$, from which position it faded away towards the violet. As the plate was panchromatic, but no record of the particular brand could be found, there was a possibility that the intensities shown on the plate might be caused mainly by the sensitising dye and not by peculiarity in the light itself. Accordingly new photographs were obtained.

The apparatus simply consisted of a silica tube through which hydrogen was passed and a silica jet through which the chlorine was admitted, the flame being started by a spark from platinum wires which could subsequently be withdrawn.

To our surprise, in addition to the continuous spectrum, a remarkable band spectrum appeared on developing the plate.

We were, at first, quite at a loss to account for this, as the only difference we could recollect was the substitution of a silica jet for the platinum jet previously used. Subsequent work, however, led to the explanation.

The flame of chlorine burning at a jet in hydrogen shows an inner portion which is livid white in tint: in our experiments this was surrounded by a cone of pale blue, which, just at the tip of the white portion, was tinged violet. In the 1924 experiment the flame was vertical, parallel to the slit; the light photographed came chiefly from the white portion, and we did not notice any blue mantle. The platinum jet was wider than the one of silica, and this caused the white portion of the flame to be broader and the blue cone (as we found later) not so big. Our photograph was taken with the flame horizontal, perpendicular to the slit; and on subsequent photographs we obtained a narrow central continuous spectrum running across the bands which extended the full length of the slit, whether the jet was of platinum or silica made no difference. Another photograph was taken in which the chlorine filled the tube and the hydrogen burnt at the jet. In this case the white flame had only a mere suggestion of an outer cone of blue; the reason for this being that the chlorine itself absorbs the light which is emitted by these violet and ultra-violet bands; for, although the maximum absorption of chlorine is not reached until λ 338 $\mu\mu$, the absorption is very considerable in the violet.

XIII.—The Hydrogen-Chlorine Flame.

By E. B. Ludlam, M.A, D.Sc., H. G. Reid, and G. S. Soutar. (With One Half-tone Plate.)

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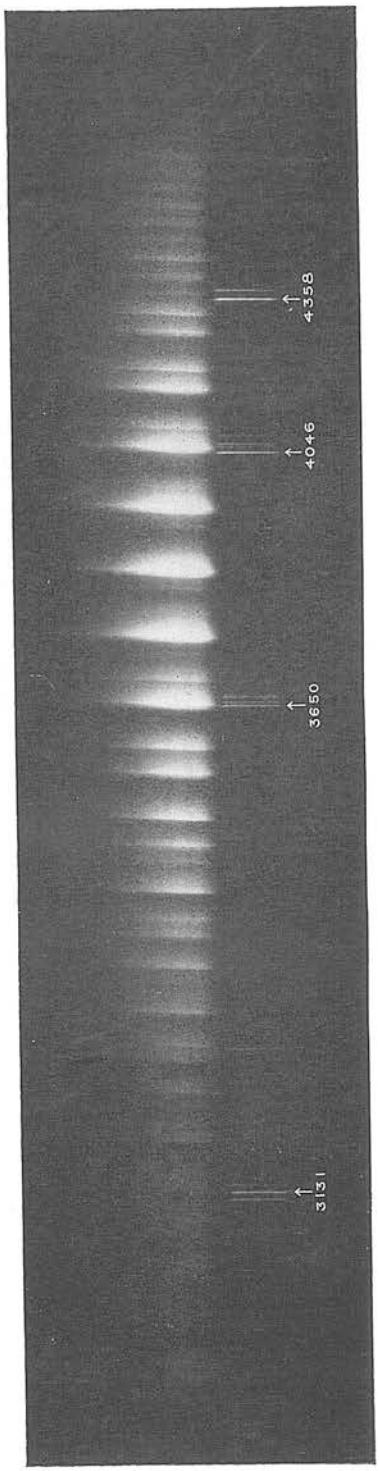
In a former paper (Ludlam and West, *Proc. Roy. Soc. Edin.*, xliv, 185) the emission spectra of the halogens in the ultra-violet region were described and discussed. In connection with the work at that time the flame produced by the union of hydrogen and chlorine was photographed in the hope of gaining some insight into the processes involved and the nature of the energy changes attending the combination. The photograph obtained showed a continuous spectrum in the visible fading rapidly in the violet.

At that time the absorption spectra of the halogens were being studied, notably by Franck and his collaborators, and rapid progress has since been made in their interpretation; but we were not then in a position to draw any important deductions from the spectrum of continuous radiation in the visible region, and our attention was directed chiefly to the continuous emission in the ultra-violet excited by the electric discharge.

Franck has shown that absorption band spectra of the halogens in the visible region all converge to a limit (Konvergenzstelle), beyond which they pass over into a continuous spectrum. This convergence limit is regarded as the position at which the energy of vibration overcomes the force holding the atoms together, and dissociation takes place into a normal and an excited atom. For chlorine this position is at λ 478 5 $\mu\mu$.

In the *Zeitschrift für Physik* for August 1928, Kondratjew and Leipunsky describe the emission spectrum of chlorine heated in a silica tube to 1000° C. Their photographs show that, in addition to the temperature radiation of the hot silica, there is an extension of the light towards the blue end of the spectrum, which they take to be the counterpart in emission of the continuous absorption studied by Franck. We have repeated these experiments and obtained similar photographs: the light from the chlorine in the tube is distinctly visible, though faint; the presumption is, that this light is emitted by the union of a normal with an excited chlorine atom.



Band Spectrum of Flame of Chlorine burning in Hydrogen containing trace of Sulphur.

in the sulphuric acid used for drying the gas. The hydrogen was originally prepared from zinc and hydrochloric acid, purified by passing through silver nitrate and alkaline permanganate to remove sulphur, but, as the sulphuric acid followed these reagents, traces of sulphur were present.

The conditions were varied by using electrolytic hydrogen which was passed over heated copper and palladised asbestos to remove traces of oxygen, and over sulphuric acid to dry the gas. The blue flame was again obtained. Addition of oxygen destroyed the colour, so that it could not be due to oxygen nor to water vapour. Assured of this, we removed the sulphuric acid drying bottle, and then failed to get the blue flame. We then added traces of sulphuretted hydrogen to the pure hydrogen, and the blue colour was obtained with much greater intensity than in any earlier experiment.

The spectrum of sulphur has been examined by a number of investigators; in particular, Johansen * has described the spectrum obtained from the cooled interior of the flame of coal gas containing sulphur. Whether, in addition to the emission from the sulphur molecule there is present in the spectrum any evidence of compounds of hydrogen, or of chlorine with sulphur, is a matter for closer examination and further experiment, including comparison with similar effects in the presence of other halogens.

We are indebted to Imperial Chemical Industries, Ltd., for the silica apparatus, and to Dr Inglis Clark, who generously presented this laboratory with the quartz spectrograph with which the later photographs were taken.

* E. S. Johansen, *Zeit. wiss. Photo.* (1912), **11**, 20–26; *cf.* also B. Rosen, *Zeit. f. Physik.* (1927), **43**, 69–130; also H. C. Urey and J. R. Bates, *Bull. Amer. Phys. Soc.*, **3**, No. 7. December 1928.

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